SOME STUDIES OF ELECTROLYTE SOLUTIONS IN LIQUID AMMONIA.

The Determination of the Transference Numbers of Some Univalent Cations at Various Temperatures.

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Thesis presented for the Degree of Doctor of Philosophy of the University of Edinburgh in the Faculty of Science.

May 1966

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INTRODUCTION

In many review articles and books which have appeared on non-aqueous solvent systems authors draw particular attention to the fact that there is a great lack of transference data in the literature, and also to the poor accuracy of most of that which does exist. Much more work is obviously needed in this direction in order to aid our understanding of solvent systems in general.

Some solvents which have received some attention in this direction are methanol and ethanol (1) (2) (3), di-methyl formamide (4), and hydrogen fluoride (5). The transference numbers of ions in some twenty three salts in liquid ammonia are obtainable from the measurements of ionic velocities made by Franklin and Cady (6), but the accuracy of their results, although the work was excellent at its time, is not up to the standards expected in modern electrochemical measurements. In addition, their work was performed at only one temperature, -34°C. In this thesis the accurate measurement of the transference numbers of a few cations at different temperatures within the normal liquid range of ammonia is described.

The transference number of an ion can be defined as the proportion of the total charge which is carried by that ion in the conduction process, thus

$$t_+ = \frac{(\frac{Necu_+}{1000})}{(\frac{Necu_+}{1000}) + (\frac{Necu_-}{1000})} = \frac{u_+}{u_+ + u_-}$$

where c is the concentration, e the charge carried by a single univalent ion and u the ionic mobility in cm./sec. when the ion is travelling down a potential gradient of 1 volt/cm.

The mobility of an ion, u, is simply related to the ion conductance, λ , by

$$\lambda = Fu$$

where F is the Faraday; and the transference number is thus related to the ion conductance by

$$t_+ = \frac{\lambda_+}{\lambda_+ + \lambda_-}$$

$$= \frac{\lambda_+}{\Lambda} ,$$

where Λ is the equivalent conductance of the salt.

Single ion conductances cannot be determined directly, for any salt must possess a minimum number of two ions which both contribute to the total salt conductance. Only when both the salt conductance and the transference number of one of the ions are known can a value for a single ion conductance be obtained.

Thus the main purpose for which transference numbers are required is for the establishment of single ion conductance and mobility data. As an ionic mobility must depend in some measure on the radius of the ion a knowledge of such a value may lead to a prediction of the size of the ion in solution.

This, in turn, gives some measure of the degree of solvation of the ion.

Apart from these important aspects, accurate transference numbers may be combined with E.M.F. data from suitable concentration cells with transference to provide activity data for ions in solution.

When a few limiting single ion conductances are known, the unknown limiting conductances of salts comprising these ions may be established. A large number of publications have been concerned with conductance data in liquid ammonia, though surprisingly few measurements have been made at temperatures other than those immediately around the boiling point of ammonia, -33.3°C. The results obtained in this work can therefore be used in the compilation of single ion conductance data when suitable salt conductance data become available.

To date, however, relatively few accurate data of important physical properties over temperatures spanning the normal liquid range of ammonia are available. For example, although Grubb, Chittum, and Hunt (7) have made fairly accurate measurements of the dielectric constant of the solvent at the boiling point and above (up to 35°C), Fish, Miller and Smyth (8) had to extrapolate their data to obtain static dielectric constants at -40° and -50°C in order to measure the relaxation times of ammonia molecules in the liquid.

The only two reports of conductance data in the literature at temperatures lower than -33°C are those of Monoszan and Pleskov (9,10) who measured the conductances of alkali metal nitrates at -40°C and that of Shatenshtein and Dykhno (11)

who measured the conductances of nitrophenols and polynitrophenols at various temperatures between +25°C. and -78°C.

The accuracy of most of the previous conductance work, with the notable exception of the classic work by Hnizda and Kraus (12), cannot be regarded as being of the same standard which is expected in modern work. Measurements, except for those of Hnizda and Kraus, have involved the dilution of the solutions being measured; the results thus depend on the measurement of volumes. For accurate work using a closed system, as is necessary with all determinations on liquid ammonia solutions, the only accurate way of determining concentrations is to distil ammonia from the solution under test and absorb the distillate to determine the weight of solvent which has been removed. In further work a system such as this will be used to determine the conductances of salts in liquid ammonia over the whole of the normal liquid temperature range.

In order to perform satisfactory extrapolations of the salt conductance, Λ_C, to infinite dilution, Λ_O, it is necessary to work at very low salt concentrations (lower than 10^{-4}M), as in a solvent ofonly moderate dielectric constant, like liquid ammonia, ion-pairing occurs to a much greater extent than in water, and even at these low concentrations deviations from the limiting laws are very significant. The paper by Hnizda and Kraus illustrates excellently the need for precise measurements at very low concentrations.

From a series of measurements of salt conductances at various concentrations, it is possible, using an extrapolation technique such as that of Fuoss and Kraus (13), to determine the salt conductance at infinite dilution Λ_o, and also the ion association constant K_A, which illustrates the tendency for the ions to associate into pairs. From such a series of measurements of the association constants, K_A, over a range of temperatures it is hoped to establish the thermodynamic functions ΔG^o, ΔH^o and ΔS^o which correspond to the ion-pairing effect. A knowledge of these functions, and in particular, ΔG^o and ΔS^o, may help to shed some light on the ion-solvent structure which exists within electrolyte solutions in liquid ammonia.

It will also be interesting, if sufficiently accurate data become available, to apply the Onsager-Fuoss treatment (14) to liquid ammonia solutions in a similar manner to that in which Kay (15) has treated the Hnizda and Kraus results.

Apart from the uses mentioned earlier to which transference numbers can be put, it is hoped that it will eventually be possible to combine the results obtained from the E.M.F.'s of suitable cells with liquid-liquid junctions in order to obtain activity coefficients, in a manner similar to that which has been described by Prue and Covington (16) for the determination of the activity coefficients of hydrogen ions in aqueous perchloric and nitric acid solutions.

If a cell such as

$$Pt/H_2 \mid NH_4Cl(c_1) \mid\mid NH_4Cl(c_2) \mid Pt/H_2$$

is set up, it will have an E.M.F. which is given by

$$E_1 = 2t_{Cl^-} \cdot \frac{RT}{F} \ln[(a_1)/(a_2)] \quad \ldots\ldots\ldots(1)$$

where c_1 and c_2 are the concentrations, and a_1 and a_2 the acivities of the solutions.

By measurement of E_1, and the use of the known transference number, important acivity data will become available. Such a method as this is a useful approach to the determination of the activity coefficients as it avoids the troublesome procedure of setting up a salt bridge in the cell, and more important, it eliminates the uncertainties which arise fromthe existence of several liquid-liquid junctions.

In this connection some experiments have already been performed in an attempt to set up a reversible hydrogen electrode in liquid ammonia solutions, all, so far, without success. There appear to be conflicting opinions in the literature regarding the performance of the hydrogen electrode in liquid ammonia. Pleskov and Monoszan (17) reported that the cell,

$$Pt/H_2 \mid NH_4NO_3(c_1) \mid\mid \text{Satd. KCl} \mid\mid NH_4NO_3(0.1\ M) \mid Pt/H_2$$

behaved reversibly at -50°C. and calculated the activities in the ammonium nitrate solutions. The results, however, deviated considerably from those calculated theoretically by

the Debye-Huckel method. On the other hand, Charret (18,19) claimed that the cell,

$Pt/H_2 \mid NH_4NO_3(c_1) \vdots$ conc. $KNO_3 \vdots NH_4NO_3(c_2) \mid Pt/H_2$

did not work because of the failure of hydrogen to absorb on to platinum black at -50°C. In view of this conflicting evidence it is important that further attempts to set up reversible hydrogen electrodes in liquid ammonia solutions must be made.

Unfortunately, fairly exhaustive studies by Heyn and Bergin (20) have established that the glass electrode does not appear to function in liquid ammonia solutions. Another approach to the determination of hydrogen ion activities might lie, however, in the use of a quinhydrone electrode system such as that described by Zintl and Neumayr (21).

Three general methods for the determination of transference numbers have been established; (i), the Hittorf method, (ii), the moving-boundary method, and (iii), the use of concentration cells with and without a liquid-liquid junction.

The third of these methods involves the use of two cells. One is set up as shown for cell (1) on page 6, and the other as,

$XCl \mid NH_4Cl(c_1) \mid H_2/Pt—Pt/H_2 \mid NH_4Cl(c_2) \mid XCl$

where XCl denotes an electrode which is reversible with respect to the chloride ion. This cell will have an E.M.F. which is given by,

$$E_2 = \frac{2RT}{F} \ln [(a_1)/(a_2)] \ldots\ldots\ldots\ldots (2)$$

A few examples of the use of this method in aqueous solutions are available (22,23,24) but its disadvantage lies in the fact that the transference numbers are given as the ratio of two slopes, thus,

$$t_+ = \frac{dE_1/d \ln a}{dE_2/d \ln a} .$$

The precise determination of the values of the slopes is very difficult, although mathematical techniques have been described (22,23). Moreover, very few satisfactory reversible electrode systems are known yet for non-aqueous solvents and a better use of the cells is undoubtedly to use the transference data obtained by other methods to provide activity data, as suggested earlier.

The Hittorf method, dating back to 1853, was the first to be introduced, and by it, much data became available in the thirty years before Arrhenius introduced the concept of the ionic theory as we now know it. The method suffers chiefly from the disadvantage that the results are obtained by analysing solutions in the electrode compartments before and after electrolysis. In order to obtain accurate results, extreme care is required in the analyses, and large changes in concentrations must occur in the two electrode compartments. If an accuracyof, say, one part in 1000 is required, then the analytical accuracy must exceed this considerably, for only a small fraction of the total number of ions can be expected to

migrate during the electrolysis. Further, even in aqueous solutions, it is difficult to find electrode systems which behave reversibly throughout the passage of the large quantity of electricity required to change appreciably the concentrations in the electrode compartments.

The method of determination of transference numbers which has become universally accepted as providing the most precise information is the moving-boundary method. This was first introduced about the turn of the century and followed on from the classic researches into the velocity of ions in gels by Sir Oliver Lodge. The first uses of the technique in solutions must be attributed to Masson (25), Steele (26) and Abegg (27), but all due credit must go to the work of Franklin and Cady (6), who first measured the velocity of ions in liquid ammonia in the summer of 1902 by means of an "autogenic" moving-boundary method.

In this method, once the boundary has been established the accuracy of the experiment depends on knowing the dimensions of the apparatus, the rate of motion of the boundary, the current passed and the concentration of the solution. All of these factors can be determined to a high degree of precision, though in a closed system, the determination of the concentration of the solution, and the filling of the transference cell both present major practical problems, which have been mainly overcome in the work described in this thesis.

Another approach, due to Kraus (28), has been made in the

attempt to establish transference numbers in non-aqueous media. This involves the assumption that a large cation and a large anion should possess essentially the same ion conductances. Using tetra-n-butylammonium triphenylborofluoride (one of these ions has 17 atoms and the other 20 atoms other than hydrogens) Kraus quoted single ion conductances for Na^+ and Br^- ions in the solvents water, liquid ammonia, pyridine, hydrogen cyanide, nitrobenzene, acetone and ethylene dichloride. A check on the technique using octadecyltrimethylammonium octadecylsulphate (29,30) produced results which agreed within five per cent of each other.

Recently Skinner and Fuoss (31) measured the conductances of sodium tetraphenylboride and triamylbutylammonium bromide in water. They found that the ion conductances were 19.69 and 20.72 respectively at 25°C., and they took the fact that the Walden products differ by only about ten per cent to indicate that the two ions behave approximately like Stokes' spheres in solution. Coplan and Fuoss (32) have studied single ion conductance data in methanol using triamylbutylammonium tetraphenylboride, and have shown that the limiting ion conductances for these ions can be given by $\Lambda_0/2$ to within one per cent. They suggest that this salt can be used as a reference electrolyte for the establishment of single ion conductance data.

There is no doubt, however, that such procedures as this can only lead to very approximate values of ion conductances,

and if accurate information is to be obtained then a direct and accurate method, such as the moving-boundary method, of determining transference numbers must be used.

Apart from the work described in this thesis the only other series of measurements leading to transference numbers in liquid ammonia which can be found in the literature is the determination of ion velocities by Franklin and Cady (6) in their early moving-boundary experiments. Although all due credit must be given to these workers their results cannot be regarded as accurate enough by modern electrochemical standards. Moreover, their measurements were limited to one temperature. They worked with uncontrolled currents and did not even integrate the current-time graphs. Their results, even after the corrections made in the paper by Kraus and Bray (33), and conversion into transference numbers do not give satisfactory plots for the extrapolation of limiting transference numbers. Even after the corrections made by Kraus and Bray, which accounted for the fact that Franklin and Cady disregarded the changing potential gradient and assumed that the degree of dissociation $\alpha = \Lambda_c/\Lambda_o$, results for ionic mobilities are available which can only be used satisfactorily to a few per cent.

In this work an experimental accuracy to give results which can be taken as accurate to better than one part in 1000 has been aimed at, and, in order to make some comparisons between cations, in the absence of all the relevant salt conductance data, the work has been carried out using nitrate solutions. A method using an "autogenic" boundary (6,34) has been devised

as this avoided the enormous practical problem which would have been created in attempting to set up a "sheared" boundary (35). Mercury was chosen as the anode metal as it can be poured into the sealed tube of the transference cell, freezes to form a good seal in the tube and electrolyses to form the soluble mercuric nitrate which acts as the indicator electrolyte. Silver was the other metal which was seriously considered for the purpose but it was found to be difficult to obtain a neat silver to glass fit when the system was to be used some 60 to 80 C. degrees below the ambient temperatures, as the two materials have different coefficients of expansion.

With experience which has been gained in the course of this work it is hoped that a much more accurate determination of the transference number of the K^+ ion in potassium iodide solution in liquid ammonia will be possible to provide a standard upon which accurate single ion conductance data can ultimately be based.

Part of the work described in this thesis has already been published (36,37).

Reprinted from CHEMICAL COMMUNICATIONS, No. 1, 13 January, 1965, Page 7.

The Mobility of the Hydrogen Ion in Liquid Ammonia

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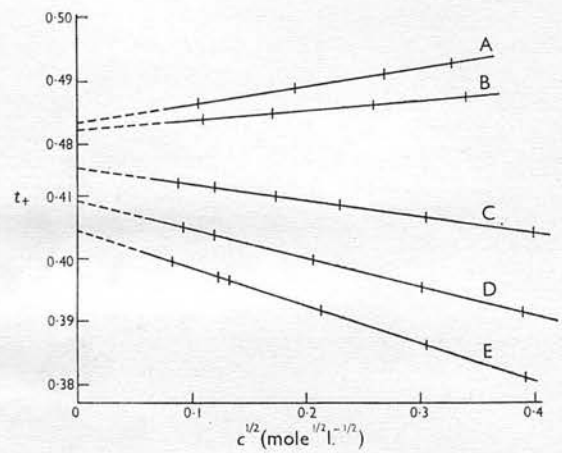
THE work of Franklin and Cady[1] indicates that the transference number of the ammonium ion (the hydrogen ion) in liquid ammonia at −34°c lies between 0·42 and 0·44. In the present work the transference numbers of ammonium and potassium ions in nitrate solutions have been determined by a moving boundary method at various concentrations up to 0·2M and temperatures between −45° and −65°. The results are shown in the Figure.

It is seen that, within the limits of the experimental error (±1 part in 1000), the transference numbers of both ammonium and potassium ions in liquid ammonia show a linear variation with $c^{\frac{1}{2}}$.



Variation of transference numbers of potassium and ammonium ions at various temperatures with the square root of concentration.

A, K^+ at −65°; B, K^+ at −48°; C, NH_4^+ at −45°; D, NH_4^+ at −55°; E, NH_4^+ at −65°.

Assuming that the nitrate ion behaves similarly in both ammonium and potassium solutions at the same concentrations and temperatures it follows that the hydrogen ion in liquid ammonia has a significantly lower ionic mobility than the potassium ion at all temperatures. Thus the phenomenon of the anomalously high ionic mobility of hydrogen ion is absent in liquid ammonia. Further the values of the transference numbers of the hydrogen ion decrease as the temperature decreases. This is exactly the opposite situation to that observed for the limiting values for the hydrogen ion in water which increase from 0·764 at 100°, to 0·830 at 25°, to 0·850 at 0°.[2] This is attributed to the increasing degree of order within the solvent's structure which allows a greater contribution towards the total mobility to come from the proton-transfer mechanism[3,4] as the temperature is lowered. The properties of molecular association within liquid ammonia are well established and in the same way an increasing degree of ordering is to be expected as the temperature decreases though not to the same extent as in water because of weaker hydrogen bonding and the inability to form three-dimensional arrangements. Thus if a proton-transfer mechanism contributes appreciably towards the ionic mobility of the hydrogen ion in liquid ammonia then an increase in the transference number relative to the nitrate ion is to be expected as the temperature is lowered. The opposite effect is observed and it is inferred, therefore, that the ionic mobility of the hydrogen ion in liquid ammonia is composed mainly of the normal mobility contribution corresponding to the diffusion of the ammonium ion and its associated solvent molecules. If a proton-transfer mechanism occurs then it must be regarded as contributing only to a minor extent towards the total ionic mobility.

(*Received, November 26th*, 1964.)

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Preprinted from the Journal of the Chemical Society,
October 1965, (1061), pages 5730—5736.

1061. *Solutions of Electrolytes in Liquid Ammonia. Part I. The Transference Numbers of Potassium, Sodium, Lithium, and Ammonium Ions in Nitrate Solutions*

By J. B. Gill

Transference numbers of K^+, Na^+, Li^+, and NH_4^+ ions in nitrate solutions in liquid ammonia have been determined at $-45°$, $-55°$, and $-65°$. Ionic mobilities are in the order $K^+ > Na^+ \simeq NH_4^+ > Li^+$, but their differences relative to each other are less than in water. The NH_4^+ ion shows no abnormal mobility properties as does the hydronium ion in water. In ammonia it differs from the NH_4^+ ion in water only in its degree of solvation relative to other ions.

Numerous reports of conductance measurements on solutions of salts in liquid ammonia have appeared in the literature. Very little of this work has been carried out at temperatures other than $-33°$, the boiling point of liquid ammonia. It is the intention in this Paper and in subsequent work to study the variations of transference numbers and conductances of salts in liquid ammonia over a range of temperatures.

A general lack of transference data in non-aqueous solutions [1,2] has hitherto made it impossible to obtain individual ion conductances and hence information about ionic sizes and solvation properties. The only data available on solutions of electrolytes in liquid ammonia are those of Franklin and Cady [3] which, although excellent at their time, only provide results at $-34°$, and these are of too low an accuracy for satisfactory extrapolation to limiting values.

The most widely accepted method for the measurement of transference numbers is the moving-boundary method. In order to avoid the very great practical difficulties which would be encountered in setting up a sheared boundary in liquid ammonia solutions, an " autogenic " boundary similar to that described by Franklin and Cady has been adopted in this work, but in which solid mercury, acting as the cell anode, was electrolysed into solution. Nitrates have been chosen as the electrolytes on account of the solubility of mercuric nitrate which acts as the indicator in liquid ammonia.

Experimental

The transference cell, shown in Figure 1 (a), consisted of a precision-bore thin-walled Pyrex glass tube A, 10 cm. long and graduated every 0·5 cm., through the lower end of which was sealed a short piece of tungsten wire B. The tube was graduated with two marks at each position so that each mark covered one quarter of the circumference, leaving clear spaces diametrically opposite each other. The tungsten, covered with a pool of mercury C, which, when frozen, served as anode, was soldered to a copper lead which was led from the cell into the glass tube D. The graduated tube A opened into a wider compartment E which contained, as the cathode compartment, a 3-cm. length of 1-cm. diameter glass tube F. The platinum cathode was mounted on a stout platinum wire which entered through the gas inlet. The ground glass joint G which carried the delivery tube was mounted concentrically with the graduated tube so that the thin delivery tube H, shown in Figure 1 (b), could be placed down to the bottom of the graduated tube to enable delivery and removal of liquid. This delivery tube was constructed from a length of thin-walled 2-mm. bore glass tubing drawn out to fit into the graduated tube as a funnel. A flexible vacuum-tight seal was made by a long rubber balloon O; this enabled the delivery tube to be inserted into and removed from the graduated tube without exposure of the contents of the cell to the atmosphere.

The thermostatted bath was an unsilvered Dewar flask containing liquid propane and a few boiling-chips sealed by a large split cork through which the cell, a spirit thermometer, and the gas outlet tube were fitted. Finally, the whole cork surface and fittings were sealed with Picene wax. A rubber band P about 5 cm. wide was fitted over the edges of the cork and the top few cm. of the Dewar flask. With this arrangement a fairly good vacuum could be maintained for a prolonged period. Constant temperatures to better than $\pm 0{\cdot}1°$ were maintained by boiling the propane under fixed reduced pressures controlled to ± 1 mm. Hg by a manostat. Temperatures were read with the spirit thermometer S which was previously calibrated against a thermocouple which could be read to better than 0·05°.

Standard solutions were prepared in the arrangement shown in Figure 1 (c). The evacuated flask L containing the weighed solid was placed in an acetone–solid carbon dioxide mixture at $-55°$ in an unsilvered Dewar flask. With the tap J closed, ammonia gas entered through the three-way stopcock K by way of the vessel M and condensed until the solution had reached the level of the graduations N in the neck of the flask. The bubbling of gaseous ammonia into the

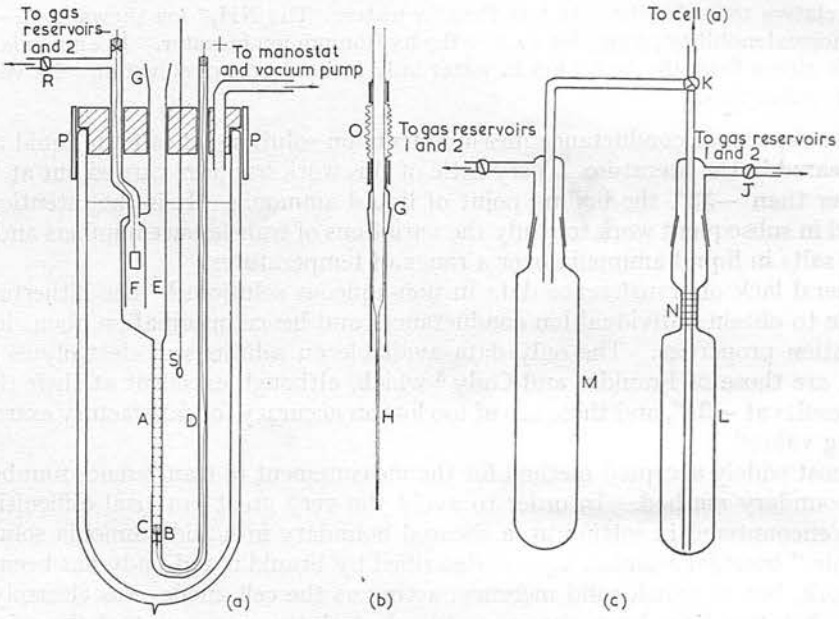

FIGURE 1. (a) Transference cell, (b) thermostatted bath, and (c) standard-flask arrangement

liquid ensured good mixing of the solutions. The flask was calibrated frequently by filling with water at 25° and weighing. A volume correction was applied to correct for the temperature at which the flask was used. No change in volume was observed with usage. When the level of solution had reached the marks N, the temperature in the surrounding Dewar flask was maintained for about 1 hr. at $-55°$ by the periodic addition of small pieces of solid carbon dioxide. Finally, the partial pressure of ammonia in the gas system was adjusted to that of the equilibrium vapour pressure [4] for the temperature of ammonia in the standard flask L. Taps K and J were now opened, the pressures over the two liquid surfaces equalised, and the volume of solutions read off.

Transfer of liquid from the standard flask L to the transference cell was effected by reducing the pressure by about 1 cm. Hg in the transference cell through gas reservoir 1. The tap K was opened to connect the standard flask to the transference cell, and, with delivery tube H inserted in the graduated tube A, the cell was filled with liquid ammonia solution. Tap K was now turned to connect the transference cell to the disposal flask M, the pressure adjusted to atmospheric in the transference cell through gas reservoir 2, and the pressure in M reduced by about 1 cm. Hg through gas reservoir 1; liquid ammonia solution was thus removed from the cell to the disposal flask M. This operation was repeated 4 or 5 times before each run to ensure

thorough washing of the cell and Polythene pipeline. Before each run the delivery tube was lifted above the level of the liquid in the cell, and the ammonia solution which it contained removed to the disposal flask. Taps K and R were then closed. Before starting a run the solution was allowed to stand in the cell for 30—45 min. to attain the temperature of the bath.

The transference cell and the standard flask were connected by 2-mm. bore thin-walled Polythene tubing, which was maintained within a few degrees of the temperature of the solution by enclosing it within a well-lagged rubber tube of $\frac{5}{8}$ in. diameter. Cold nitrogen gas, supplied from a sealed Dewar flask containing a heating coil, was passed through the rubber jacket, and the temperature was controlled by adjustment of the current supply to the heater.

The gas lines connecting the two gas reservoirs, the transference cell, and the standard flask were guarded from the atmosphere by moisture and carbon dioxide traps. The gas reservoirs, about 5-l. capacity, could be isolated independently or interconnected to enable the equalisation of pressures.

A potential difference about 100v d.c. was applied across the cell. This was supplied from a constant-current device similar to that described by Hopkins and Covington [5] but based on a constant 650v d.c. source provided by a Solartron power pack, type AS 1165. The current was measured potentiometrically through a manganin-wound standard resistance of 10 ohms in series with the cell.

The graduated tube A was calibrated with mercury. Differences in the mercury levels and the adjacent marks were compared against the differences in weights. Calibrations were made over minimum tube distances of 4 cm. (8 marks) with a cathetometer which could be read to $\pm 0{\cdot}001$ cm.

Preparation of Materials.—All the salts except lithium nitrate were of AnalaR quality and were recrystallised three times and dried in a vacuum over phosphoric oxide for several days. They were then stored in desiccators over phosphoric oxide. Lithium nitrate was recrystallised five times and dried in a vacuum over phosphoric oxide at room temperature for 1 week. Finally, it was dried for 3 weeks at 61° in a vacuum over phosphoric oxide. The water contents of all the salts used were no higher than trace quantities. When in use the salts were stored in a vessel connected through a side-arm to a vessel containing phosphoric oxide. This device had a ground-glass joint which fitted the neck of a weighing bottle narrow enough to fit into the neck of the standard flask L. Contact of the salts with the atmosphere was thus reduced to only a few seconds during each weighing.

The ammonia used was distilled once from a cylinder of pure anhydrous ammonia. Titrations of the water contents of samples by Karl Fischer reagent by a procedure similar to that developed by Hodgson and Glover [6] showed the moisture content to be less than 0·005%.

Errors.—Current measurements were better than 1 part in 3000, and the cell calibration better than 1 part in 4000. The time at which the boundary passed a mark in the cell could be established to ± 1 sec., and all the times used in the calculation of results were greater than 2000 sec. Temperature coefficients of the transference numbers of K^+, Na^+, Li^+, and NH_4^+ ions are 0·0002, 0·0006, 0·0004, and 0·0005 per °c, respectively. As temperatures were controlled to $\pm 0{\cdot}1°$, the errors due to any variation in temperature were negligible. The greatest likely source of error was in the evaporation of ammonia during the transference of the solution from the standard flask to the cell. During this process the pressure was reduced by about 1 cm. Hg below atmospheric. If the maximum distillation occurred, then the error due to evaporation would be about 1 part in 1200 at $-55°$.

In the absence of molar-volume data for the ions, no corrections have been made for volume changes in the solutions during electrolysis; these are likely to be small. The correction due to the specific conductance of the ammonia is negligible. An accuracy of $\pm 0{\cdot}1\%$ is claimed for the results.

Results

In all cases mercuric ions electrolysed very well into solution from the solid mercury anode, and before the first graduation was reached a clear sharp thin flat boundary had been obtained. Except for ammonium nitrate, the boundaries became difficult to observe at concentrations much below 0·01M.

Transference numbers were compiled from the equation $t_+ = VcF/1000IT$, where V is the volume swept out in time T, c is the concentration in moles per litre, and F is the Faraday. In each run a series of 30—40 values of V and T were obtained. From these results the standard

deviations obtained rarely exceeded 0·0003 in t_+, and maximum variations in individual results 0·0008 in t_+.

Concentrations were calculated in molar units, assuming that the ratio of the densities of the solutions were the same as the ratio of the densities of liquid ammonia over the same temperature range. The density data of Cragoe and Harper [7] were used.

An early series of experiments indicated that there was no variation in t_+ with the potential difference applied, and subsequently runs were designed in which the boundary moved 5 cm. in 2000—3000 sec.

Values obtained in the individual experiments are given in Table 1, except that the results for K^+ ion at −45·0° have been extrapolated from a series of results obtained at −48·0°.

TABLE 1

Variation of t_+ with concentration

KNO_3 (−65·0°)		$NaNO_3$ (−65·0°)		$LiNO_3$ (−65·0°)		NH_4NO_3 (−65·0°)		KNO_3 (−55·0°)	
t_+	c	t_+	c	t_+	c	t_+	c	t_+	c
0·4928	0·10736	0·3902	0·10860	0·3443	0·10355	0·3814	0·15645	0·4907	0·10761
0·4915	0·07285	0·3942	0·05413	0·3544	0·05185	0·3864	0·09430	0·4890	0·07190
0·4893	0·03647	0·3973	0·02567	0·3630	0·02281	0·3914	0·04659	0·4877	0·04203
0·4869	0·01129	0·3995	0·01430			0·3964	0·01796	0·4849	0·01042
		0·4004	0·01145			0·3969	0·01581		
						0·3994	0·006420		

NH_4NO_3 (−55·0°)		KNO_3 (−45·0°)		$NaNO_3$ (−45·0°)		$LiNO_3$ (−45·0°)		NH_4NO_3 (−45·0°)	
0·3918	0·15156	0·4875	0·11413	0·4013	0·09643	0·3524	0·10199	0·4054	0·15916
0·3954	0·09193	0·4857	0·06762	0·4057	0·05315	0·3670	0·03530	0·4071	0·09331
0·3997	0·04498	0·4861	0·06092	0·4074	0·03557	0·3692	0·02852	0·4086	0·05212
0·4037	0·01452	0·4840	0·02839	0·4092	0·02301	0·3725	0·01930	0·4101	0·03136
0·4051	0·008932	0·4825	0·01210	0·4116	0·01214			0·4114	0·01445
								0·4117	0·007896

It was originally intended to include the transference numbers of the cæsium ion in this work. However, the maximum solubility of cæsium nitrate in liquid ammonia at these temperatures was about 0·01M. With such a low solubility the concentration range over which the variation of t_+ can be observed was far too small to allow satisfactory extrapolation of plots of t_+ against $c^{\frac{1}{2}}$ to limiting values.

DISCUSSION

The plots of t_+ against $c^{\frac{1}{2}}$ for all the ions studied are linear, within the limits of experimental error, as seen in Figure 2 (a—d), and the values of the limiting transference numbers, t_+°, shown in Table 2 were obtained by linear extrapolations. From the results in Table 2, values of the limiting cation conductances relative to the limiting conductance of the nitrate ion can be obtained from the relationship $\Lambda_+^\circ/\Lambda_-^\circ = t_+^\circ/(1 - t_+^\circ)$.

The absolute values of Λ_+° are not obtainable in the absence of conductance data. They are, however, proportional to the values of the ratio $\Lambda_+^\circ/\Lambda_-^\circ$, shown in Table 3, since Λ_-° refers to the nitrate ion in all cases, and it is this ratio which is used in this Paper to compare limiting cation conductances.

TABLE 2

Limiting cation transference numbers in nitrate solutions in liquid ammonia at various temperatures

Temp.	K^+	Na^+	Li^+	NH_4^+
−65·0°	0·4842	0·4052	0·3794	0·4040
−55·0	0·4824	—	—	0·4092
−45·0	0·4805	0·4170	0·3880	0·4140

TABLE 3

Limiting ion conductances in liquid ammonia ÷ $\Lambda_{NO_3^-}^\circ$

Temp.	K^+	Na^+	Li^+	NH_4^+
−65·0°	0·939	0·681	0·611	0·678
−55·0	0·932	—	—	0·692
−45·0	0·925	0·715	0·634	0·707

The limiting conductance of the ammonium ion, regarded as the hydrogen ion in liquid ammonia, is seen to be approximately equal to that of the sodium ion and less than that of the potassium ion at all temperatures. Thus, the mobility of the hydrogen ion in liquid ammonia is not anomalous as it is in aqueous solutions. Moreover, there is little change with temperature in the ratio $\Lambda_{M^+}^\circ/\Lambda_{NH_4^+}^\circ$, where M^+ is alkali-metal ion. Certainly, there is no change which can be compared with the change in the ratio $\Lambda_{M^+}^\circ/\Lambda_{H^+}^\circ$ in water over a range of temperature, as can be seem from a comparison in Tables 4 and 5.

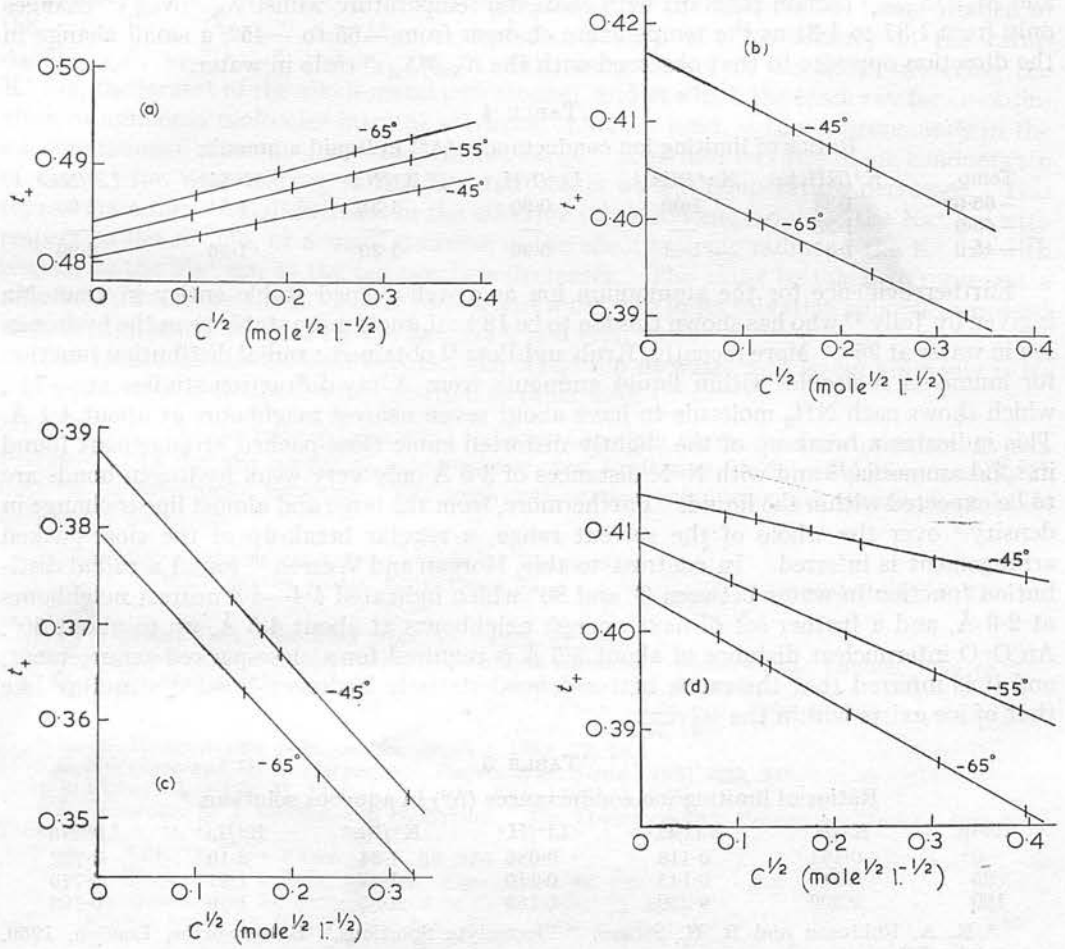

FIGURE 2. Variation of the transference numbers of univalent cations with the square root of concentration at various temperatures in liquid ammonia: (a) K^+ in KNO_3; (b) Na^+ in $NaNO_3$; (c) Li^+ in $LiNO_3$; (d) NH_4^+ in NH_4NO_3

In aqueous solutions the high mobility of the hydrogen ion is attributed to the proton-transfer mechanism [8,9] in which a proton passes, in the direction of the applied field, from a charged hydronium ion to an uncharged arrangement of associated water molecules by the making and breaking of a hydrogen bridge. The properties of molecular association in liquid ammonia are well established, and with considerable hydrogen-bonding an increasing degree of ordering must occur as the temperature decreases, though not to the same extent as in water because of the weaker hydrogen-bonding between the nitrogen atoms and the inability for ammonia to form the three-dimensional arrangements found in water. There appear to be similar structural conditions in ammonia, and the transference of charge by a proton-transfer process seems feasible though to a lesser extent than in water on account of the reduced number of transfer sites available.

If a proton-transfer mechanism contributes appreciably to the mobility of the hydrogen ion in ammonia, it is to be expected that its contribution will increase with decrease in temperature as the degree of molecular association within the solvent increases. The pronounced increase in mobility of the hydrogen ion in water with decreasing temperature relative to the other ions can be seen from Table 5 by the change in the ratios $\Lambda_{K^+}^\circ/\Lambda_{H^+}^\circ$, $\Lambda_{Na^+}^\circ/\Lambda_{H^+}^\circ$, and $\Lambda_{Li^+}^\circ/\Lambda_{H^+}^\circ$. The similar ratios involving the NH_4^+ ion in liquid ammonia show no such trend with change of temperature. In ammonia the ratios $\Lambda_{Na^+}^\circ/\Lambda_{NH_4^+}^\circ$ and $\Lambda_{Li^+}^\circ/\Lambda_{NH_4^+}^\circ$ remain constant with changing temperature whilst $\Lambda_{K^+}^\circ/\Lambda_{NH_4^+}^\circ$ changes only from 1·37 to 1·31 as the temperature changes from −65 to −45°, a small change in the direction opposite to that observed with the $\Lambda_{K^+}^\circ/\Lambda_{H^+}^\circ$ ratio in water.

TABLE 4

Ratios of limiting ion conductances (Λ°) in liquid ammonia

Temp.	K^+/NH_4^+	Na^+/NH_4^+	Li^+/NH_4^+	K^+/Na^+	K^+Li^+	Li^+/Na^+
−65·0°	1·38	1·00	0·90	1·38	1·54	0·90
−55·0	1·35	—	—	—	—	—
−45·0	1·31	1·01	0·90	1·30	1·46	0·90

Further evidence for the ammonium ion as a well-defined stable entity in ammonia is given by Jolly [10] who has shown this ion to be 18 kcal./mole more stable than the hydrogen ion in water at 25°. More recently, Kruh and Petz [11] obtained a radial distibution function for ammonia molecules within liquid ammonia from *X*-ray diffraction studies at −74°, which shows each NH_3 molecule to have about seven nearest neighbours at about 4·1 Å. This indicates a break-up of the slightly distorted cubic close-packed arrangement found in solid ammonia,[12] and with N–N distances of 3·6 Å only very weak hydrogen bonds are to be expected within the liquid. Furthermore, from the large and almost linear change in density [7] over the whole of the solvent range, a regular break-up of the close-packed arrangement is inferred. In contrast to this, Morgan and Warren [13] found a radial distibution function in water between 0° and 80° which indicated 4·4—4·8 nearest neighbours at 2·9 Å, and a further set of next nearest neighbours at about 4·5 Å, up to about 30°. An O–O internuclear distance of about 3·5 Å is required for a close-packed arrangement, and it is inferred that the much better defined strongly hydrogen-bonded structure like that of ice exists within the solvent.

TABLE 5

Ratios of limiting ion conductances (Λ°) in aqueous solutions *

Temp.	K^+/H^+	Na^+/H^+	Li^+/H^+	K^+/Na^+	K^+/Li^+	Li^+/Na^+
0°	0·181	0·118	0·086	1·54	2·10	0·732
25	0·210	0·143	0·110	1·47	1·91	0·770
100	0·309	0·230	0·183	1·35	1·70	0·793

* R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," Butterworths, London, 1959, appendix 6.2.

It must therefore be concluded that the transport mechanism of the hydrogen ion in liquid ammonia is predominantly that of the normal mobility contribution corresponding to the diffusion of the ion and its associated solvation sphere through the solvent.

The order of ionic mobilities in liquid ammonia is $K^+ > Na^+ \approx NH_4^+ > Li^+$, and in water is $K^+ \approx NH_4^+ > Na^+ > Li^+$. The differences between ionic conductances in liquid ammonia and in water can best be seen by comparing the ratios $(\Lambda_{Na^+}^\circ - \Lambda_{Li^+}^\circ)/\Lambda_{Na^+}^\circ$ and $(\Lambda_{K^+}^\circ - \Lambda_{Na^+}^\circ)/\Lambda_{Na^+}^\circ$. These are 0·10 and 0·23, and 0·30 and 0·47, at −65° and 25°, respectively, indicating that with reference to the Na^+ ion there are greater diffrences between the mobilities of K^+ and Li^+ ions in water than in liquid ammonia. Thus, the effective solvated ionic radii have smaller differences relative to each other in liquid ammonia than in water, and there is a smaller change in the degree of solvation in passing through the series.

The ions Li^+, Na^+, and NH_4^+ all form fairly stable uni-univalent ammoniated salts in

the liquid-ammonia temperature range. This indicates strong co-ordination by ammonia molecules to the cation in all cases except K^+ ion. A well-defined primary solvation sphere around the cation is inferred, but the tendency of ions to arrange the solvent molecules into a secondary solvation sphere is likely to be much less in ammonia with its weaker hydrogen-bonding ability. It is therefore most probable that the ion conductances and ion mobilities observed in liquid ammonia correspond much more nearly to those of a primary solvation sphere than is the case with water.

From Table 4 it is seen that there is constancy over the temperature range studied in the ratios $\Lambda_{Na^+}{}^\circ/\Lambda_{NH_4^+}{}^\circ$, $\Lambda_{Li^+}{}^\circ/\Lambda_{NH_4^+}{}^\circ$, and $\Lambda_{Li^+}{}^\circ/\Lambda_{Na^+}{}^\circ$, but inconstancy in the ratios $\Lambda_{K^+}{}^\circ/\Lambda_{NH_4^+}{}^\circ$, $\Lambda_{K^+}{}^\circ/\Lambda_{Na^+}{}^\circ$, and $\Lambda_{K^+}{}^\circ/\Lambda_{Li^+}{}^\circ$. Only in the cases of the ratios involving the K^+ ion, the largest of the alkali-metal ions studied, and in which the tendency for co-ordination of ammonia molecules into the solvation sphere is least, is there inconstancy in the ion conductance ratios over the temperature range. A greater increase in ion conductance of the K^+ ion with respect to the Na^+ ion occurs as the temperature decreases. This represents either a small increase in the effective solvated ionic radius of the Na^+ ion with respect to the K^+ ion, or a small decrease in the effective ionic radius of the K^+ ion with respect to the Na^+ ion as the temperature decreases. This must be taken to represent a reduced influence by the K^+ ion on the solvent molecules in its solvation spheres compared with the influences exerted by the Li^+, Na^+, and NH_4^+ ions.

The great difference found between the NH_4^+ ion in water and liquid ammonia is its much greater degree of solvation relative to other ions.

The author thanks Imperial Chemical Industries Limited for the loan of equipment, British Petroleum Ltd. for the supply of pure propane, and Professors Sir Edmund Hirst and T. L. Cottrell for laboratory facilities. The work was carried out during the tenure of an I.C.I. Research Fellowship.

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Printed in Great Britain by Richard Clay (The Chaucer Press) Ltd.,
Bungay, Suffolk.

RESULTS

The results of the transference number measurements of the alkali metal and ammonium ions in liquid ammonia solutions of nitrates at -45°C, -55°C and -65°C are shown in Tables 1, 2 and 3.

The results shown for the K^+ ion at -45°C in Table 1 have been obtained by extrapolation of the plot of the change in transference number with temperature for fixed concentrations of salt. For this purpose the results obtained at the temperature of -48°C (shown at the beginning of Appendix I) have been used along with the results shown in Tables 2 and 3. The temperature coefficients of the transference numbers of the K^+ ion are very small and the consequent errors involved in the extrapolation are negligible.

The concentrations studied covered the range 0.008 M to 0.15 M. The dilute end of this range was the lower limit at which the boundary could be observed satisfactorily, and the upper limit of concentration was governed by the dimensions of the apparatus, the time required to perform an experiment and the current supply which was required.

In all cases mercuric ions electrolysed very well into solution from the solid mercury anode and before the first graduation was reached a clear sharp boundary had been established. At the lower concentrations the boundaries were most well-defined in the electrolyses of ammonium nitrate solutions, and with the other salts it was impracticable to perform experiments at concentrations lower than 0.01 M.

Table 1

Variation of the transference numbers of cations with concentration (c mole.$l.^{-1}$) in liquid ammonia solutions of nitrates at $-45^{o}C$.

	K^+			NH_4^+	
c	t_+	σ	c	t_+	σ
0.11413	0.4875	0.0006	0.15916	0.4054	0.0005
0.06762	0.4857	0.0004	0.09331	0.4071	0.0004
0.06092	0.4861	0.0004	0.05212	0.4086	0.0003
0.02839	0.4840	0.0006	0.03136	0.4101	0.0007
0.01210	0.4825	0.0004	0.01445	0.4114	0.0004
			0.007896	0.4117	0.0007

	Na^+			Li^+	
c	t_+	σ	c	t_+	σ
0.09643	0.4013	0.0005	0.10199	0.3524	0.0003
0.05315	0.4057	0.0003	0.03530	0.3670	0.0003
0.03557	0.4074	0.0004	0.02852	0.3692	0.0004
0.02301	0.4092	0.0004	0.01930	0.3725	0.0003
0.01214	0.4116	0.0010			

Table 2

Variation of the transference numbers of cations with concentration (c mole.l^{-1}) in liquid ammonia solutions of nitrates at -55°C.

	K^+			NH_4^+	
c	t_+	σ	c	t_+	σ
0.10761	0.4907	0.0006	0.15156	0.3918	0.0005
0.07190	0.4890	0.0003	0.09193	0.3954	0.0003
0.04203	0.4877	0.0005	0.04498	0.3997	0.0004
0.01042	0.4849	0.0003	0.01452	0.4037	0.0003
			0.008932	0.4051	0.0004

Table 3

Variation of the transference numbers of cations with concentration (c mole.l.$^{-1}$) in liquid ammonia solutions of nitrates at -65°C.

K^+			NH_4^+		
c	t_+	σ	c	t_+	σ
0.10736	0.4928	0.0007	0.15645	0.3814	0.0003
0.07852	0.4915	0.0003	0.09430	0.3864	0.0004
0.03647	0.4893	0.0005	0.04659	0.3914	0.0003
0.01129	0.4869	0.0009	0.01796	0.3964	0.0003
			0.01581	0.3969	0.0004
			0.006420	0.3994	0.0005

Na^+			Li^+		
c	t_+	σ	c	t_+	σ
0.10860	0.3902	0.0008	0.10355	0.3443	0.0003
0.05413	0.3942	0.0004	0.05185	0.3544	0.0003
0.02567	0.3973	0.0004	0.02281	0.3630	0.0004
0.01430	0.3995	0.0007			
0.01145	0.4004	0.0004			

The values of the transference numbers were determined from the equation,

$$t_+ = \frac{V\ c\ F}{1000\ I\ T},$$

where V ml. is the volume swept out by the boundary in time T seconds, I is the current in milliamps and c is the molar concentration.

With between 30 and 45 values of V and T in each experiment, values of the standard deviation, σ, of the results within each experiment have been obtained. These also have been collected into Tables 1, 2 and 3, and are shown for each value of t_+.

The values of the concentrations shown in the above tables have been calculated by making the reasonable assumption that the ratio of the densities of the liquid ammonia solutions over a range of temperatures is the same as the ratio of the densities of pure liquid ammonia over the same range of temperatures. This procedure was checked for aqueous salt solutions and found to give accurate values of concentrations at various temperatures. It was necessary to calculate concentrations in this way because all the solutions were made up and transferred within the apparatus at $-55.0 \pm 0.2^{\circ}C$. The density data used for these calculations are shown in Appendix II.

EXPERIMENTAL ERRORS

The currents supplied to the transference cell by the constant current device described on page 81 were found to be constant to about one part in 3000. The constancy was determined by measurement of the potential drop across standard resistances of 1.0160 and 10,000 ohms by means of a vernier potentiometer. The resistances had been previously standardised using a digital voltmeter and a standard Weston cadmium cell.

The calibration of the transference cell at 25°C by weighing mercury turned out to be one of the more precise calibrations performed on the equipment. The cathetometer used could be read to ± 0.001 cm. Distances along the moving-boundary tube of less than 4.0 cm. were not used in the calculation of results from the experiments. Consequently, errors greater than one part in 4000 were unlikely in the determination of the positions of marks more than 4.0 cm. apart on the moving-boundary tube. The volume between any two adjacent marks was determined by weighing the mercury removed between the marks, the measuremnts being carried out at 25° ± 0.2°C. Errors in these weighings were negligible, for the weight of mercury removed between any two marks was of the order of 0.5 g., and this was weighed by difference on a micro-balance to give a weight accurate to ± 0.00001 g. Final checks on the accuracy of the calibrations were made by comparing the weights of mercury removed from longer lengths of the tube (e.g., 10 - 15 marks) with the volumes calculated

from the previous calibration. The two sets of results agreed very well and the calibration of the moving-boundary tube was accepted as accurate to one part in 4000 at 25°C. A volume correction to the temperature at which the apparatus was used was applied after the calculation of the transference numbers. This correction is seen to be only just significant, as follows;

Linear coefft. of expansion of Pyrex glass	= 3.6×10^{-6},
Volume " " " " " "	= 1.08×10^{-5}.
Volume change of 1 ml. at -45°C	= 0.0007 ml.
" " " 1 ml. at -55°C	= 0.0008 ml.
" " " 1 ml. at -65°C	= 0.0009 ml.

In spite of the requirement that the solutions in liquid ammonia must be made up in a closed system, their concentrations could be determined with a very high degree of accuracy. All weighings of the solid samples were made to better than 0.00001 g. and the lowest weights used were greater than 0.1 g. The standard flask was calibrated with water (about 140 g.) and this was weighed to within 0.002 g. on a beam balance. (All the weights used in the work had been previously calibrated against a master set). A correction for the volume of air contained in the flask during the weighing without water was included in the final calculation of the volume of the flask. Errors in the other measurements made in the course of this calibration were negligible. For example, the volumes between the marks in the neck of the flask were determined by means of

a dropping pipette and were correct to ± 0.01 ml. The largest possible error in the measurement of the volume of glass in the dip-pipe (measured by micrometer-screw gauge prior to construction) was about two per cent, representing an error of ± 0.02 ml. Thus the accuracy placed on the determination of the volume of the standard flask was better than one part in 3000. All experimental solutions were prepared at -55°C and a volume correction of 0.12 ml. was deducted from the measured volume at 25°C to give the volume at -55°C.

The times at which the boundary passed the graduations on the moving-boundary tube could be determined by eye to within one second. In nearly every experiment the boundary was very sharp - better than is normally obtained in moving-boundary experiments in water. Therefore, it was considered unnecessary to construct an optical aid to detect the position of the boundary as the minimum period of time from which any one result was calculated was about 2000 seconds and this measurement was not considered to be the greatest source of error in the work.

Temperature control in the experiments was aimed at maintaining the thermostatted bath to within 0.1 C. degree. Occasionally temperatures did vary more widely than this, but only on one occasion did the temperature vary by as much as 0.25 C. degree. It was considered that poor temperature control might affect the experiments in two possible ways. Firstly, the speed of the boundary might change because of the change in the value of the cation conductance, λ_+, with respect

to the value of the anion conductance, λ_-, thus affecting the value of t_+. Secondly, the quality of the boundary could be affected by the creation of convection currents within the liquid in the cell. These, if great enough, could even destroy a boundary altogether. The former of these factors was insignificant in the experiments studied, for, if the temperature coefficients of the transference numbers are calculated from the results shown in Tables 1, 2 and 3 for the ions concerned, they are found to be K^+, 0.0002; Na^+, 0.0006; Li^+, 0.0004; and NH_4^+, 0.0005 per C. degree. As the temperature control was to $\pm$0.1 C. degree, the variation in transference number due to temperature can be neglected. Moreover, when such sharp well-defined boundaries were obtained and maintained throughout the experiments, it must be assumed that convection effects within the cell were very small.

The greatest likely source of error resulted from the transfer of the liquid ammonia solutions from the standard flask to the transference cell. During this process the solution was exposed to a slightly reduced pressure in order to effect a siphon, and although the pressure differential was not allowed to become greater than 1.5 cm. Hg (usually about 1.0 cm.Hg) the gas volume above the siphon was about 5 litres. This source of error was made most apparent in the course of the preliminary experiments in which the disposal flask was not placed at a controlled temperature of $-55^{\circ}C$, but was left at atmospheric temperature. As this flask was connected to the same gas reservoirs as the standard flask and transference cell,

considerable distillation of ammonia occurred to and from the disposal flask during the transference of solutions. Spurious results were obtained and these were attributed to the lack of control over the concentrations of the measured solutions. When the disposal flask containing a small volume of liquid ammonia was placed in a constant temperature bath at -55°C (acetone - solid carbondioxide mixture) such distillations were greatly reduced and much better control over the concentrations of the solutions during transference was achieved with much better consistency in the results for the transference numbers. The error due to the distillation of the solvent during transfer of solutions has been estimated as follows.

The transfer of solution from the standard flask to the transference cell involves the reduction of the pressure above the liquid in the cell by about 10 mm.Hg, in order to effect the siphon. In this process the partial pressure of ammonia vapour at -55°C above the liquid in the cell is reduced to $225 \times \frac{750}{760} = 222.0$ mm. Hg. If it is assumed that distillation of ammonia from the transference cell occurs to replace half of the ammonia lost from the gas reservoir during the transfer of the solution, then the second transfer of wash-solution will start with a partial vapour pressure of ammonia in the gas reservoir of 223.5 mm. Hg.

Similarly, the second transfer of liquid involves a reduction

of the partial vapour pressure of ammonia in the gas reservoir from 223.5 mm. to $223.5 \times \frac{750}{760} = 220.5$ mm. Hg. If a similar distillation of half the ammonia required to replace that removed from the gas reservoir occurs, then the third transfer of liquid will commence with a partial pressure of ammonia vapour in the transference cell of 222.75 mm. Hg. Similarly the fourth transfer of solution will commence with a partial pressure of ammonia vapour in the transference cell of 222.4 mm. Hg.

If it is now assumed that, after the fourth transfer of solution, the maximum distillation of ammonia occurs to establish a saturated ammonia atmosphere within the gas reservoir, thus raising the partial pressure of ammonia from 222.4 mm. to 225.0 mm. Hg in a volume of 5 litres, then the volume of ammonia gas which distils from the sample solution is about 20 ml. at N.T.P. (about 0.015 g.). The volume of solution from which this ammonia distils is about 25 ml. (about 17.5g.). Thus the error in the concentrations of the solutions calculated in this manner is about one part in 1200.

The above calculation is based on rather crude approximations but it is felt that the actual error due to the distillation of ammonia from solutions during the transfer process is likely to be less than has been calculated above. On the other hand, the very worst possible case must be considered. That is the case in which it is assumed that there is no distillation of ammonia into the gas reservoir between the transfer processes, and that there is a maximum distillation

of ammonia vapour after the last transfer of solution (i.e., after the test solution is in the transference cell. In this situation, the maximum possible error is calculated to be one part in 450.

After considerations of the times during which the ammonia solutions being transferred were in contact with the atmosphere of the gas reservoir, and the fact that immediately after the last transference of the test solution this atmosphere was closed off to prevent further distillation, a reasonable estimate of the maximum possible error from this source would seem to be one part in 1200.

As the effect of temperature on the value of the transference numbers was relatively small, no special regard was paid to the accurate measurement of temperature. Thermometers were all of the spirit type and the one mounted in the cell assembly was calibrated against a chromel-alumel thermocouple which had itself been previouslycalibrated to ±0.05 C. degree by the measurement of standard temperatures. Temperatures read on the spirit thermometers were estimated to ±0.1C. degree.

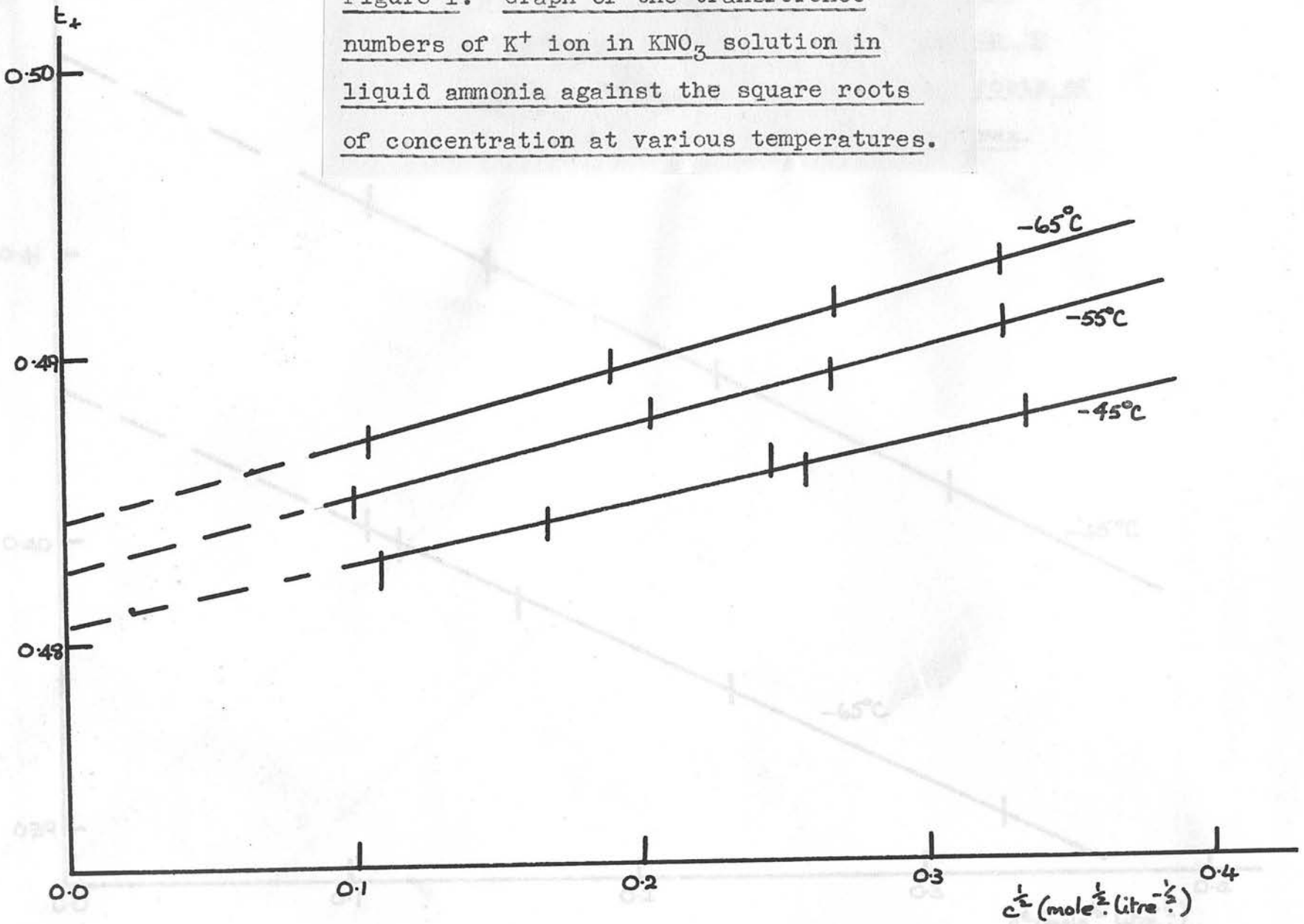
It was pointed out by Longsworth (38, 39) that the observed value of a transference number is dependent to a small extent on a contribution to the conductivity by the solvent and also to changes in the volume of the solution during electrolysis due to the change in density of the solutions as the indicator ions replace those under observation. These effects may be equated as follows,

$$t_{true} = t_{observed} + \Delta t_{solvent} + \Delta t_{MV}$$

In the case of ammonia the intrinsic conductivity of the solvent (12,40) is extremely low and must be regarded as negligible at the concentrations studied. (The conductivity of liquid ammonia is much less than that of water and corrections in aqueous solutions amount to about 0.0001 in the value of t_+ for the most dilute solutions in which the conductivity contributions from the water is most apparent).

There is no molar volume data in the literature for the Hg^{++} ion in liquid ammonia solutions, and until this is available the second correction accounting for the change in volume of the solutions cannot be carried out. It is, therefore, hoped that these corrections will be small.

Figure 1. Graph of the transference numbers of K^+ ion in KNO_3 solution in liquid ammonia against the square roots of concentration at various temperatures.



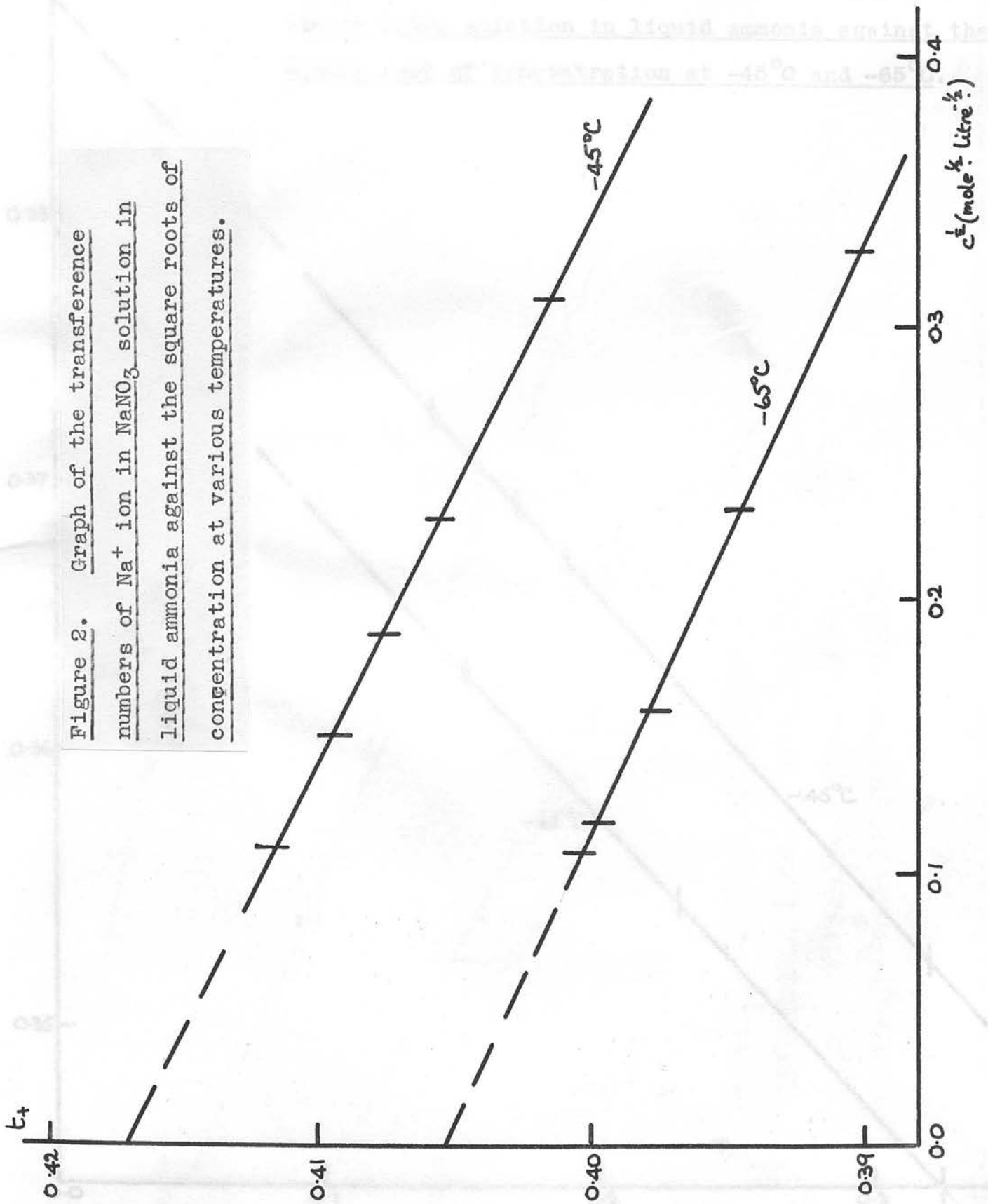


Figure 2. Graph of the transference numbers of Na^+ ion in $NaNO_3$ solution in liquid ammonia against the square roots of concentration at various temperatures.

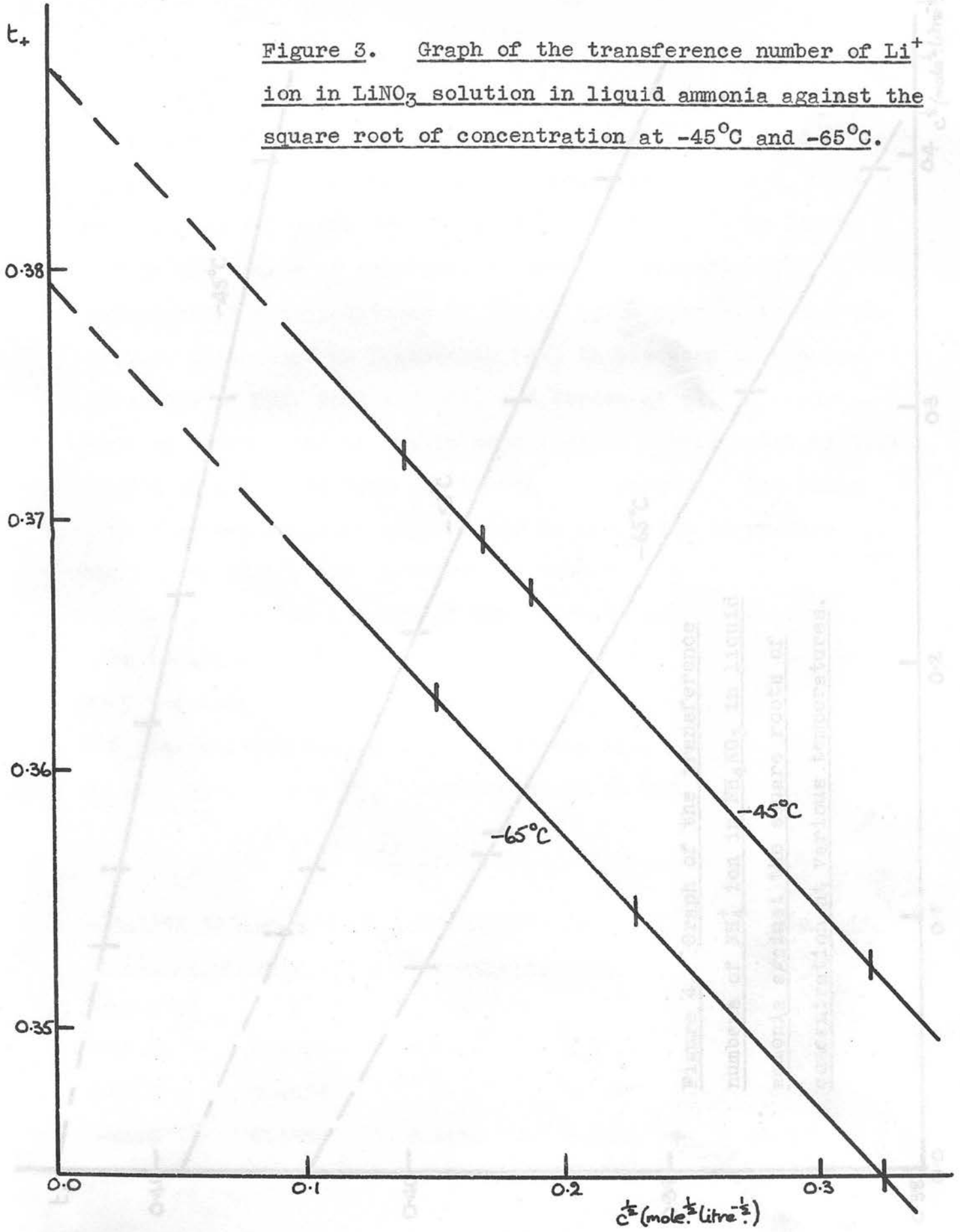


Figure 3. Graph of the transference number of Li^+ ion in $LiNO_3$ solution in liquid ammonia against the square root of concentration at -45°C and -65°C.

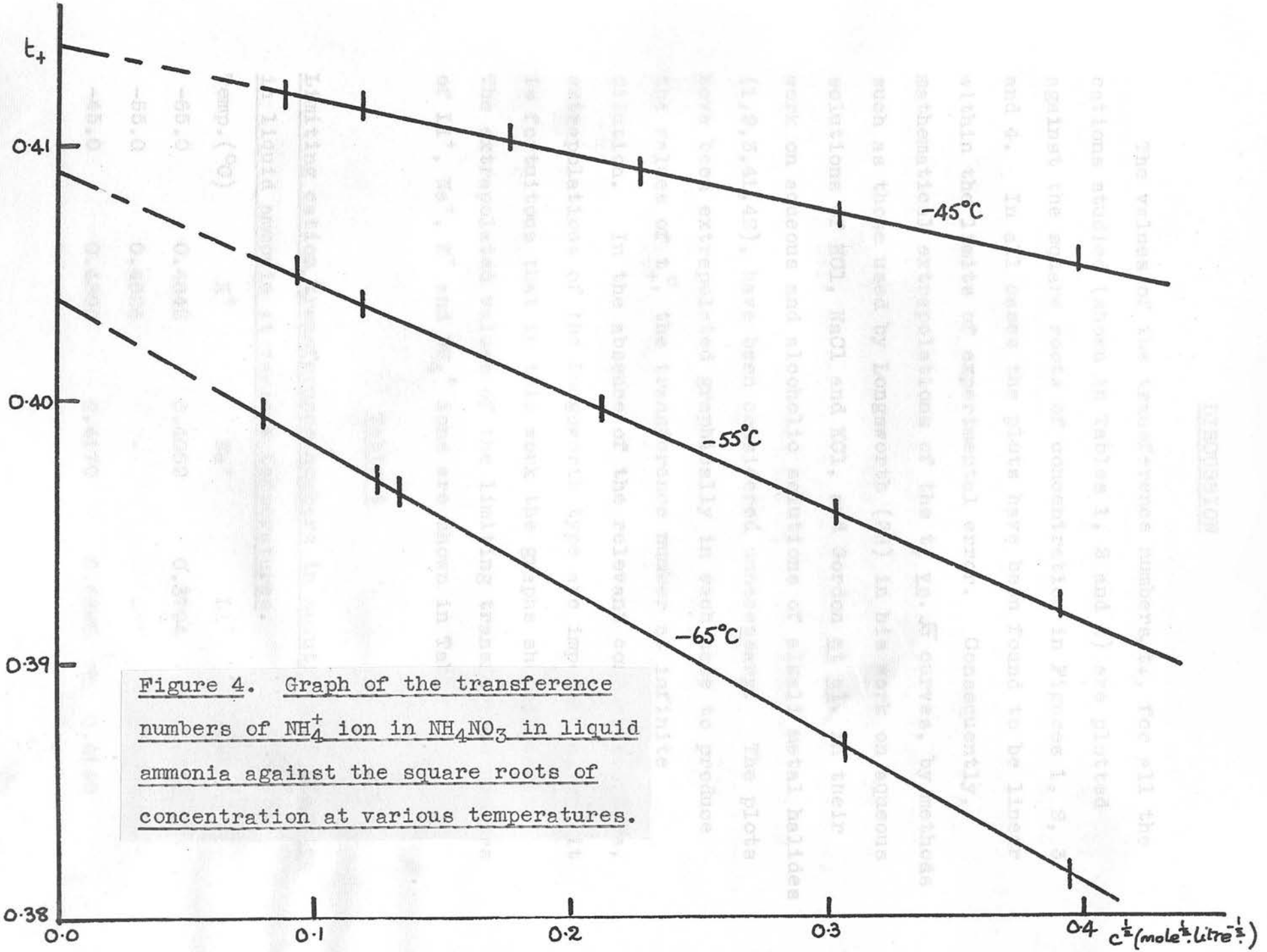


Figure 4. Graph of the transference numbers of NH_4^+ ion in NH_4NO_3 in liquid ammonia against the square roots of concentration at various temperatures.

DISCUSSION

The values of the transference numbers, t_+, for all the cations studied (shown in Tables 1, 2 and 3) are plotted against the square roots of concentration in Figures 1, 2, 3 and 4. In all cases the plots have been found to be linear within the limits of experimental error. Consequently, mathematical extrapolations of the t_+ *vs.* $\sqrt{c}$ curves, by methods such as those used by Longsworth (38) in his work on aqueous solutions of HCl, NaCl and KCl, and Gordon *et al.* in their work on aqueous and alcoholic solutions of alkali metal halides (1,2,3,41,42), have been considered unnecessary. The plots have been extrapolated graphically in each case to produce the values of t_+^o, the transference number at infinite dilution. In the absence of the relevant conductance data, extrapolations of the Longsworth type are impossible, and it is fortuitous that in this work the graphs show linearity. The extrapolated values of the limiting transference numbers of Li^+, Na^+, K^+ and NH_4^+ ions are shown in Table 4.

Table 4

Limiting cation transference numbers in solutions of nitrates in liquid ammonia at various temperatures.

Temp.(°C)	K^+	Na^+	Li^+	NH_4^+
-65.0	0.4842	0.4052	0.3794	0.4040
-55.0	0.4824	-	-	0.4092
-45.0	0.4805	0.4170	0.3880	0.4140

Comparatively few single ion conductance data are available in the literature and those there are are based on the transference data from the work of Franklin and Cady (6) in 1902. Some individual results quoted may also be based on the modifications made to these results by Kraus and Bray (33). However, all these results refer to the temperature at which Franklin and Cady carried out their experiments, namely -34°C., and the results presented in this work are claimed to be the first on any salt solutions in liquid ammonia at temperatures lower than this. In the absence of conductance data it is impossible to obtain the values of individual ion conductances, but as long as solutions containing the same anion are compared, ratios of the individual ion conductances of the cations can be obtained.

In the limiting case where the law of independent migration can be applied,

$$\Lambda^{\circ} = \lambda_{+}^{\circ} + \lambda_{-}^{\circ}$$

and $$t_{+}^{\circ} = \frac{\lambda_{+}^{\circ}}{\Lambda^{\circ}}$$

$$= \frac{\lambda_{+}^{\circ}}{\lambda_{+}^{\circ} + \lambda_{-}^{\circ}}$$

therefore $$\frac{\lambda_{+}^{\circ}}{t_{+}^{\circ}} = \lambda_{+}^{\circ} + \lambda_{-}^{\circ}$$

and $$\lambda_{+}^{\circ} = t_{+}^{\circ}\lambda_{+}^{\circ} + t_{+}^{\circ}\lambda_{-}^{\circ}$$

thus $$\lambda_{+}^{\circ} = \left(\frac{t_{+}^{\circ}}{1 - t_{+}^{\circ}}\right) \cdot \lambda_{-}^{\circ} \qquad \ldots\ldots\ldots\ldots\ldots\ldots (3)$$

If the anion remains unchanged then the limiting anion conductance λ°_{-} appears as a constant in equation (3) and the values of the limiting conductances of the ions can be compared without prior knowledge of any conductance values. In this work nitrate was chosen as the anion mainly on account of the high solubility of nitrate solutions in liquid ammonia.

Comparisons of this kind are only valid at infinite dilution when the influence of one ion upon the ion conductance of another ceases to exist. It would be incorrect to compare the conductances of two cations at any one particular concentration for it is impossible to say what influence the nitrate ion has on the conductance of the individual cations and vice versa.

For a series of cations in nitrate solution the values of the term $t^{\circ}_{+}/(1 - t^{\circ}_{+})$ are proportional to the values of the limiting cation conductances and these are compared in Table 5.

Table 5

Limiting ion conductances in liquid ammonia $\div \lambda^{\circ}_{NO_3^-}$

Temp.($^{\circ}$C)	K^+	Na^+	Li^+	NH_4^+
-65.0	0.939	0.681	0.611	0.678
-55.0	0.932	-	-	0.692
-45.0	0.925	0.715	0.634	0.707

It is clearly seen from Table 5 that the limiting ion conductances and consequently the limiting ion mobilities, which are proportional, are in the order $K^+ > Na^+ \approx NH_4^+ > Li^+$. Table 6

shows the corresponding values of the limiting ion conductances in water over a range of temperatures (43).

Table 6

Limiting ion conductances in water at various temperatures

($cm.^2 ohm^{-1} equiv.^{-1}$)

Temp. (^oC)	K^+	NH_4^+	Na^+	Li^+	H^+
0	40.7	40.2	26.5	19.4	225
25	73.5	73.6	50.1	38.6	350
100	195	180	145	115	630

The order of ionic mobilities in water is seen to be $K^+ \approx NH_4^+ > Na^+ > Li^+$, being similar to that in liquid ammonia except in the case of the ammonium ion which moves more slowly in liquid ammonia with respect to the sodium ion than in water. This would appear to be contrary to expectation as the ammonium ion is well accepted as being the solvated form of the hydrogen ion in liquid ammonia (44) and might be expected to possess some properties of anomalously high mobility such as that possessed by the hydrogen ion in aqueous solutions.

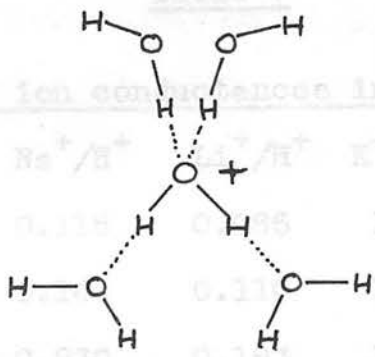
The phenomenon of high proton mobility in aqueous solutions has been explained in terms of a proton-transfer mechanism (45,46,47) in which the proton is transferred from a protonated water species to a non-protonated water species in the direction of the field:

In order to promote a proton transfer, two rate determining steps are involved:

(1) rate of orientation of the water species so that an O·····H——O arrangement is in the right direction,

(2) the transfer of the proton over the O·····H——O linkage - a low activation energy has been given by Wirtz and Gierer (48) as 2.4 Kcal., and by Loewenstein and Szoke (49) as 2.6 ± 0.3 Kcal.

A hydrated proton is perhaps better described as the $H_4O_9^+$ species in which the four available hydrogen-bonding sites of the central O atom are occupied by O·····H——O bonds, thus;



This species would be expected to have a similar mobility to the K^+ ion as it has a similar size to the K^+ ion solvated by four water molecules. Thus the excess mobility of the solvated proton above that of the normal mobility due to the diffusion of the species through the solvent is to be regarded as the contribution of the proton-jump mechanism to the total mobility.

The lower the temperature of the solution the more highly solvated will this system become, and the more highly solvated will the water species become. As the intra-molecular rearrangement of charge is to be regarded as almost instantaneous,

the more highly associated species will give rise to higher contribution to the mobility of the proton from the proton-transfer mechanism. Thus in aqueous solutions the contribution of the proton transfer mechanism to the ion conductance is seen to become increasingly important as the temperature decreases and the solvent becomes more highly associated. The effect is illustrated in Table 7, in which some ratios of limiting ion conductances in water at 0°, 25° and 100°C are given. If the case of the K^+ ion is considered, and it is assumed that this ion is

Table 7

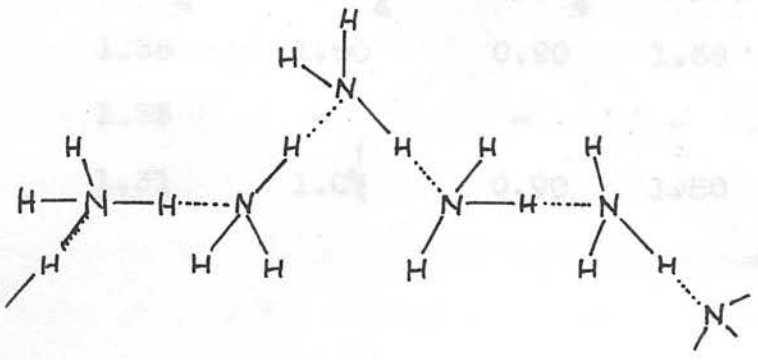
Ratios of limiting ion conductances in aqueous solution

Temp.(°C)	K^+/H^+	Na^+/H^+	Li^+/H^+	K^+/Na^+	K^+/Li^+	Li^+/Na^+
0	0.181	0.118	0.086	1.54	2.10	0.732
25	0.210	0.143	0.110	1.47	1.91	0.770
100	0.309	0.230	0.183	1.35	1.70	0.793

surrounded by four solvating water molecules, then the crystallographic size will be very similar to that of the $H_4O_9^+$ species. Thus from size considerations the contributions to the mobility of the two species in water corresponding to the diffusion of the ions through this solution should be closely comparable. The first column of Table 7 illustrates that this is not the case, as the total ion conductance of the H^+ ion is almost three times as great as the K^+ ion even at 100°C. What

is most significant is the great increase in mobility of the H^+ ion with respect to the K^+ ion as the temperature decreases, until at 0^oC the ion conductance of H^+ is some 5.5. times greater than that of the K^+ ion. This phenomenon clearly indicates the increase in the contribution of the proton-transfer mechanism to the total ionic mobility of the H^+ ion as the temperature decreases and the solvent acquires a much more well-defined strongly hydrogen-bonded structure like that of ice.

Liquid ammonia possesses an abnormally high latent heat of vapourisation, and an abnormally high boiling point when compared with the other hydrides of Group V elements. This is usually taken to indicate a high degree of association within the liquid through hydrogen-bonding, and with considerable hydrogen-bonding an increasing degree of ordering of the solvent is expected to occur as the temperature decreases. This will not occur to the same extent as in water for two reasons. Firstly, ammonia molecules with only one "lone pair" of electrons and three hydrogen atoms are incapable of forming the three-dimensional ice-like network proposed for water, and the most likely form of association will consist of linear chains of the form



Secondly, the hydrogen-bonding with longer N—H····N distances than O—H····O will be markedly weaker. These considerations lead to the conclusion that the right solvent conditions appear to exist in liquid ammonia for a proton-transfer mechanism to occur, but that if it does then it will be to a much lesser extent than in water. Previous work involving the conductances of ammonium salts in liquid ammonia (50,51) failed to produce evidence of abnormal proton mobility (52). However, all previous work has been performed at temperatures near the boiling point of liquid ammonia where the number of hydrogen-bonded species is likely to be at a minimum. No results are available in the literature for temperatures covering the lower and middle portions of the liquid temperature range.

The ratios of the limiting ion conductances in liquid ammonia are shown in Table 8. It can be seen that over the temperature range -65°C to -45°C the ratio between the limiting ion conductances of the NH_4^+ ion and the K^+ ion changes only slightly. If a significant

Table 8

Ratios of limiting ion conductances in liquid ammonia

Temp.(°C)	K^+/NH_4^+	Na^+/NH_4^+	Li^+/NH_4^+	K^+/Na^+	K^+/Li^+	Li^+/Na^+
-65.0	1.38	1.00	0.90	1.38	1.54	0.90
-55.0	1.35	-	-	-	-	-
-45.0	1.31	1.01	0.90	1.30	1.46	0.90

proton-transfer mechanism contributed to the mobility at the lower temperatures then it would be expected that the ratio would decrease markedly with decreasing temperature. Instead, a small change occurs in the opposite direction from 1.31 to 1.38. Furthermore, the ratios $\lambda^{\circ}_{Na^+}/\lambda^{\circ}_{NH_4^+}$ and $\lambda^{\circ}_{Li^+}/\lambda^{\circ}_{NH_4^+}$ remain constant over this temperature range. As the limiting ion conductance of the NH_4^+ ion is almost precisely the same as that of the Na^+ ion over the temperature range studied it must be concluded that the NH_4^+ ion in liquid ammonia behaves "normally" and any appreciable proton-transfer mechanism which occurs must be regarded as insignificant.

Further evidence which indicates that the NH_4^+ ion is a well-defined stable entity in liquid ammonia has been given by Jolly (53) who suggested that this ion is 18 Kcal./mole more stable in liquid ammonia than is the solvated proton in water.

Little structural information was available on liquid ammonia until Kruh and Petz (54) recently obtained a radial distribution function for the ammonia molecules in liquid ammonia from X-ray diffraction studies at $-74^{\circ}C$. They found each nitrogen atom to have about seven nearest neighbours at about 3.6 Å. and a further four next nearest neighbours at 4.1 Å. Recently Olavsson and Templeton (55), in a study of the crystal structure of solid ammonia found that the nitrogen atoms are arranged in a slightly distorted close-packed arrangement so that each nitrogen atom has six nearest N-neighbours at 3.6 Å. and a further six next nearest N-neighbours at 3.9 Å. Furthermore, these workers showed

that the hydrogen atoms do not lie in the direct line of centres of the N—N distances. In such an arrangement the hydrogen-bonding must be regarded as extremely weak.

The work of Kruh and Petz appears to suggest that the liquid is formed from the melting crystals by a straightforward break-up of the solid ammonia crystals, so that the liquid at a few degrees C. above its freezing point is still showing substantially the same structure as the solid. Therefore, it must be inferred that, if the N—N distances in the liquid are 3.6 Å. or greater, the hydrogen-bonding system will be very weak - much more so than in water. In the aqueous system, Morgan and Warren (56) obtained a radial distribution function which indicates that, between 0° and 80°C., an oxygen atom has 4.4 to 4.8 nearest oxygen neighbours at 2.9 Å. and between 0° and 30°C., a further set of next nearest oxygen neighbours at 4.5 Å. A close-packed arrangement of water molecules requires an internuclear O—O distance of about 3.5 Å. and it is clear that the more open and better-defined strongly hydrogen-bonded structure like that of ice exists within the liquid.

Further support towards the great differences between the structures of water and liquid ammonia is given by considering the changes in densities with temperature. Water exhibits the phenomenon of maximum density at 4°C. which is attributed to the partial breakdown of the open-lattice structure of ice. No such phenomenon has been reported for

liquid ammonia. The density data due to Cragoe and Harper (57) show an almost linear change in density with temperature over the whole of the liquid range (see Appendix II). The change of density is very large compared with that of water for it changes from 0.7314 g./ml. at -75°C. to 0.6838 g./ml. at -35°C., a change of 7.0 per cent in 40 C. degrees. In water, the rate of change in the density is at its maximum in the upper temperature range of the liquid. Here the density changes in a non-linear manner from 0.9832 to 0.9584 g./ml. from 60° to 100°C. (some 2.5 per cent in 40 C. degrees), a very much smaller change (58), even though this is the temperature range over which the density of water changes most rapidly. These facts indicate the smaller hydrogen-bonding strength in liquid ammonia and the much lower proportion of a well-defined associated species in the liquid.

Therefore, it must be concluded that the ammonium ion in liquid ammonia does not exhibit a proton-transfer mechanism in the conduction process at any temperature (if it does, then its contribution is insignificant) and that its mobility is predominantly that of the normal mobility contribution corresponding to the diffusion of the ion and its associated solvation sphere through the solvent.

One significant fact which emerges is that the mobility of the NH_4^+ ion in liquid ammonia is significantly lower with respect to the other alkali metals than it is in water. For instance, the limiting conductance is almost identical in

water with that of the K^+ ion at all temperatures, whereas in liquid ammonia it is almost identical with that of the much less mobile Na^+ ion at all temperatures. This may be taken to mean that the NH_4^+ ion, together with its solvating solvent molecules (the first layer of which will be expected to be attached by N—H·····N bonds), is essentially the same size as the solvated Na^+ ion.

In other respects the order of mobilities in liquid ammonia and water are the same although the magnitudes of the mobilities of ions differ between the solvents. The best comparison of ion conductances between water and liquid ammonia is given by considering the ratio of the differences between ion conductances and a particular ion, say that of Na^+. Table 9, which has been compiled from Tables 5 and 6, shows these ratios such as $(\lambda^\circ_{Na^+} - \lambda^\circ_{Li^+})/\lambda^\circ_{Na^+}$ for various temperatures in liquid ammonia and water. This table shows that there are

Table 9

	Liquid ammonia			Water	
	$\left(\frac{\lambda^\circ_{Na^+} - \lambda^\circ_{Li^+}}{\lambda^\circ_{Na^+}}\right)$	$\left(\frac{\lambda^\circ_{K^+} - \lambda^\circ_{Na^+}}{\lambda^\circ_{Na^+}}\right)$		$\left(\frac{\lambda^\circ_{Na^+} - \lambda^\circ_{Li^+}}{\lambda^\circ_{Na^+}}\right)$	$\left(\frac{\lambda^\circ_{K^+} - \lambda^\circ_{Na^+}}{\lambda^\circ_{Na^+}}\right)$
-65°C	0.103	0.379	0°C	0.268	0.536
-45°C	0.110	0.294	25°C	0.228	0.467
			100°C	0.207	0.345

greater differences between the mobilities of the ions in water than in liquid ammonia. For instance, the ratio $(\lambda^\circ_{K^+} - \lambda^\circ_{Na^+})/\lambda^\circ_{Na^+}$ is 0.38 at -65°C. in liquid ammonia and 0.54 and 0.47 in water

at 0° and 25°C. respectively. Similarly the other ratios are smaller in liquid ammonia than in water, indicating that, with reference to the Na^+ ion, greater differences are to be found between the mobilities of the K^+ and Li^+ ions in water than in liquid ammonia. This means that the effective solvated ionic radii must have smaller differences with respect to each other in liquid ammonia than in water, and that there is a smaller change in the degree of solvation in passing through the series.

The ions Li^+, Na^+ and NH_4^+ all form fairly stable ammoniated salts in the liquid ammonia temperature range (59). An example is given by $NaCl.5\frac{1}{2}NH_3$, the structure of which has recently been described by Olavsson (60). Fairly strong co-ordination to the cations is indicated in all cases except the K^+ ion, for which no ammoniates have been described. The inference is that the cation in solution acquires a well-defined primary solvation sphere, but the tendency of the ions to extend their effect to the solvent molecules and organise them into a secondary solvation sphere, as is the case in aqueous solutions, is small. This is understandable as ammonia molecules only form weak hydrogen-bonds. It is, therefore, very probable that the ion conductances and mobilities observed in liquid ammonia refer very much more nearly to those of an ion surrounded by a primary solvation sphere than is the case in water.

Reference to Table 8 shows that the limiting ion conductance ratios, $\lambda^\circ_{Na^+}/\lambda^\circ_{NH_4^+}$, $\lambda^\circ_{Li^+}/\lambda^\circ_{NH_4^+}$ and $\lambda^\circ_{Na^+}/\lambda^\circ_{Li^+}$ are constant

over the temperature range studied. It is significant that the ion conductance ratios involving the K^+ ion, $\lambda^\circ_{K^+}/\lambda^\circ_{NH_4^+}$, $\lambda^\circ_{K^+}/\lambda^\circ_{Na^+}$ and $\lambda^\circ_{K^+}/\lambda^\circ_{Li^+}$ show inconstancy and that the K^+ ion, the largest of the alkali metal ions studied, shows the least tendency for co-ordination. With respect to the Na^+ ion, a greater increase in the ion conductance of the K^+ ion occurs as the temperature decreases. This may be accounted for in two ways. Either there is a small increase, with respect to the K^+ ion, in the effective ionic radius of the Na^+ ion as the temperature decreases, or there is a small decrease, with respect to the Na^+ ion, in the effective ionic radius of the solvated K^+ ion. In view of the lack of evidence in favour of strong co-ordination of solvent molecules to the K^+ ion, it seems more reasonable to choose the second of these two possibilities, and the effect must be taken as representing a reduced influence by the K^+ ion on the solvent molecules in its solvation sphere, compared with the influences exerted by the Li^+, Na^+ and NH_4^+ ions.

The above argument presupposes that a law similar in form to Stokes' law is true for ions in solution. In a solvent it is unlikely that an ion will behave according to Stokes' law (61),

$$F = 6\pi r \eta u ,$$

where F is the force exerted on the ion, r is its radius, η is the coefficient of viscosity of the solvent and u is the velocity of the ion through the medium. The ion may be of irregular shape and will be under the influence of the enormous

electrical forces which exist between molecules and ions over molecular distances and under conditions where it is impossible to predict the dielectric constant of the immediate environment of the ion. It is possible that a similar law operates in which the numerical constant is changed,

$$F = k\, r \eta\, u\ .$$

If such a law holds then a method exists by which the radius (the Stokes' radius) of the species may be related to the ionic mobility, since F, k and η may all be taken as constants.

Thus

$$r \propto \frac{1}{u_+}$$

and since u_+ is proportional to λ_+,

$$r^o \propto \frac{1}{\lambda^o_+}\ .$$

It is important to remember, however, that even large ions can show deviations from Stokes' law as illustrated by Kraus (62) and this type of treatment must be used with extreme caution.

As Table 5 provides values which are proportional to the limiting ion conductances for the ions studied in this work, it is possible to provide some indication in the trends in the Stokes' radii. These are shown in Table 10, in which X, Y and Z are constants.

Table 10

Trends in the Stokes' radii of Li^+, Na^+, K^+ and NH_4^+ ions in liquid ammonia.

Temp.(°C)	Li^+	Na^+	K^+	NH_4^+
-65.0	1.65X	1.47X	1.06X	1.47X
-55.0	-	-	1.07Y	1.45Y
-45.0	1.58Z	1.41Z	1.08Z	1.42Z

With the appropriate conductance data Table 10 could be completed with actual numerical values, but the ratios given can, none the less, be used to show the changes in sizes of the ions with change of temperature. When the temperature decreases, the radii of Li^+, Na^+ and NH_4^+ ions increase, whereas, depending on the values of X and Z (and these are uncertain since, apart from fundamental constants, they also depend on λ_- and η°), the K^+ ion radius increases to a smaller extent.

Greater reliability could be placed on this data if it were known that Walden's rule (63), or some similar relation, was obeyed by the solutions over the temperature range, and it is hoped that sufficient data will eventually become available to test this.

Consideration of the graphs in Figures 1, 2, 3 and 4 provides an interesting comparison between aqueous solutions and liquid ammonia solutions. The results of the transference numbers of K^+, Na^+ and Li^+ ions in their aqueous chloride solutions (38,64,65) may be plotted against the square roots

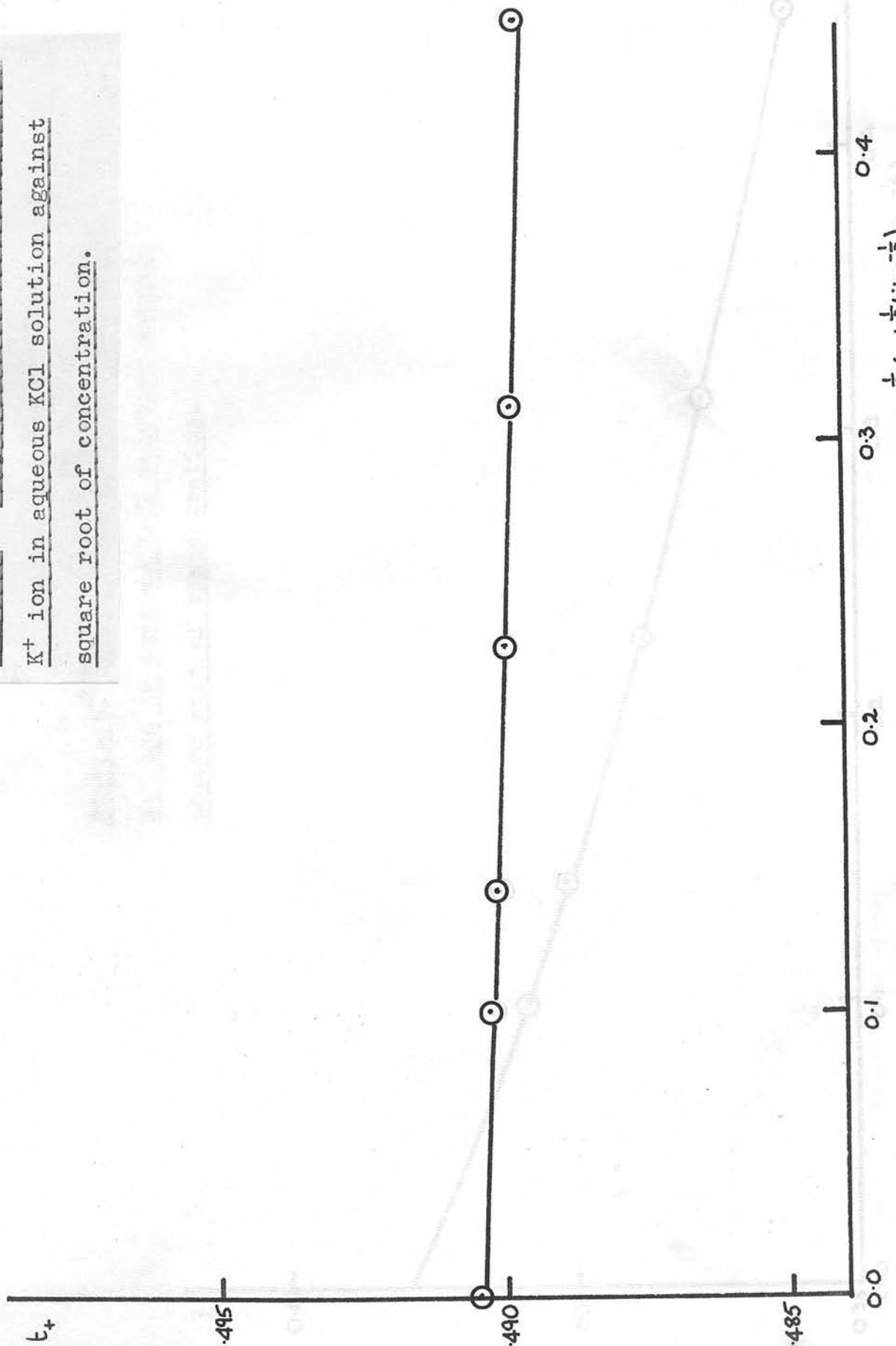
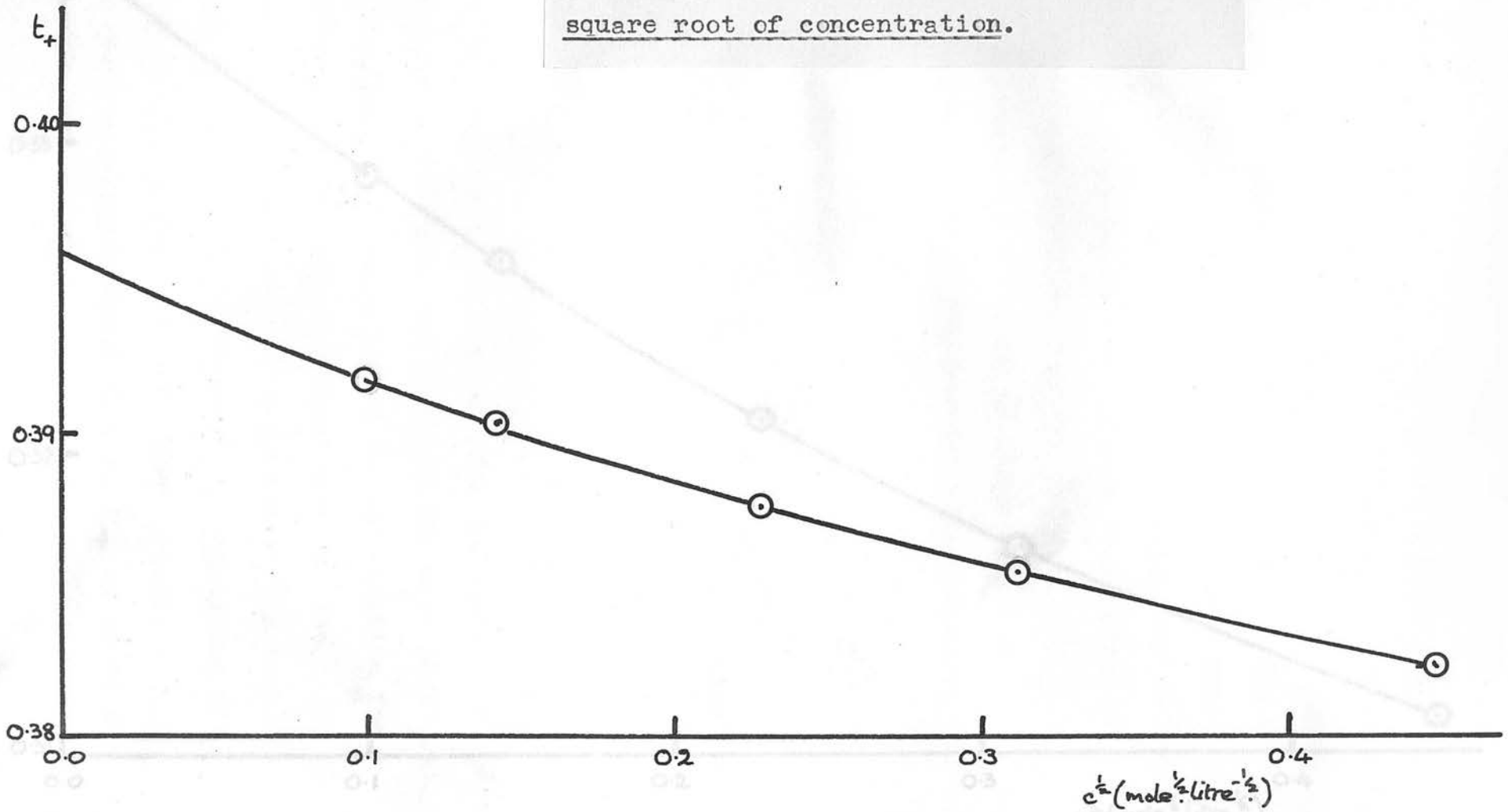


Figure 5. Graph of transference number of K^+ ion in aqueous KCl solution against square root of concentration.

Figure 6. Graph of transference number of Na^+ ion in aqueous NaCl solution against square root of concentration.



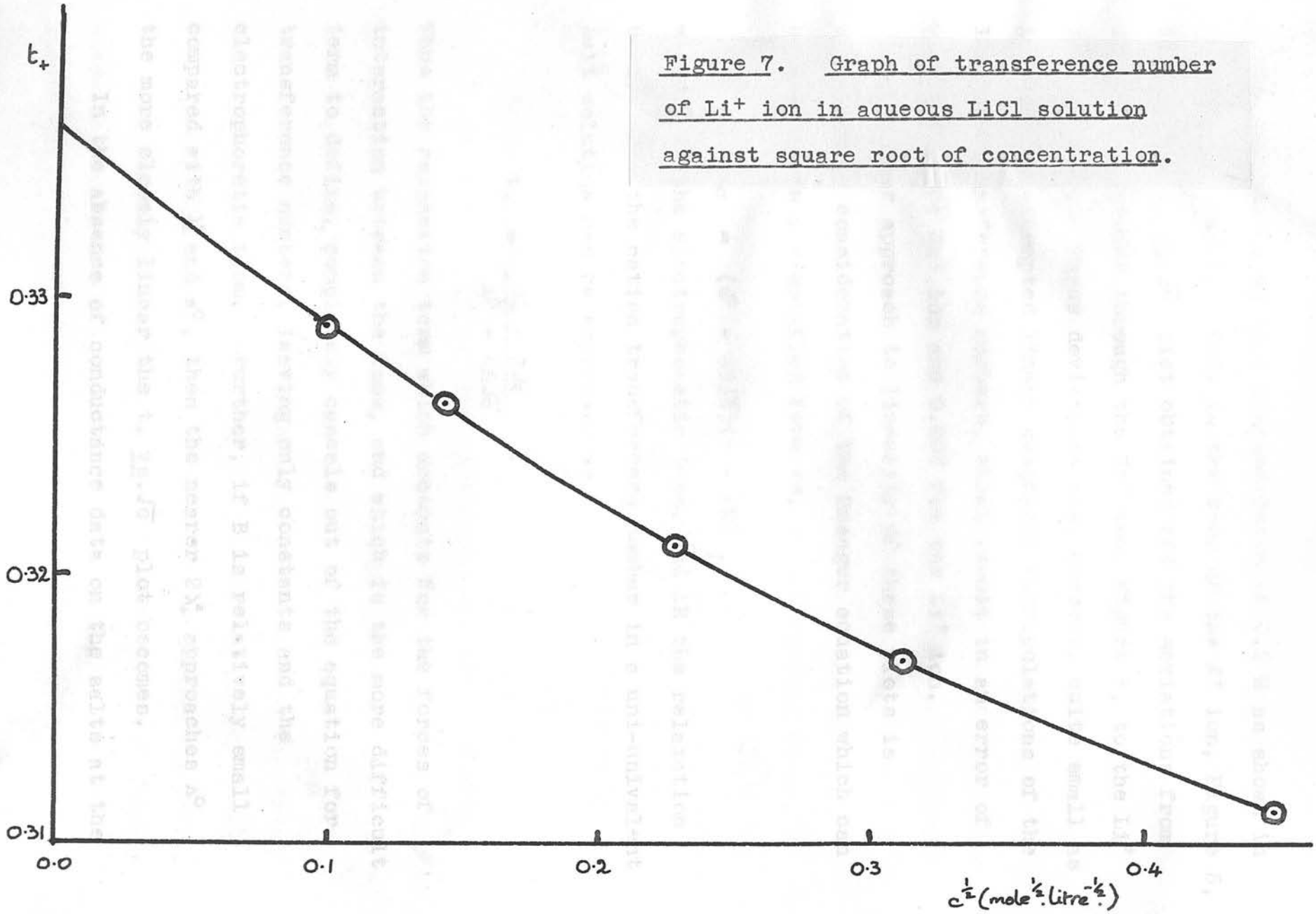


Figure 7. Graph of transference number of Li^+ ion in aqueous LiCl solution against square root of concentration.

of concentrations up to a concentration of 0.2 M as shown in Figures 5, 6 and 7. Only in the case of the K^+ ion, Figure 5, is a linear t_+ *vs.* $\sqrt{c}$ plot obtained and the deviations from linearity increase through the Na^+ ion, Figure 6, to the Li^+ ion, Figure7. These deviations are, however, quite small as is shown by attempted linear graphical extrapolations of the limiting transference numbers, which result in an error of 0.0015 for the Na^+ ion and 0.003 for the Li^+ ion.

The near approach to linearity of these plots is explained by consideration of the Onsager equation which can be written in a simplified form as,

$$\Lambda_c = (\Lambda^o - 2B\sqrt{c})(1 - \Delta R) ,$$

where B is the electrophoretic term, and ΔR the relaxation term. Now the cation transference number in a uni-univalent salt solution can be expressed as,

$$t_+ = \frac{\lambda_+^o - B\sqrt{c}}{\Lambda^o - 2B\sqrt{c}} .$$

Thus the relaxation term which accounts for the forces of interaction between the ions, and which is the more difficult term to define, completely cancels out of the equation for transference numbers, leaving only constants and the electrophoretic term. Further, if B is relatively small compared with λ_+^o and Λ^o, then the nearer $2\lambda_+^o$ approaches Λ^o the more closely linear the t_+ *vs.* $\sqrt{c}$ plot becomes.

In the absence of conductance data on the salts at the

temperatures studied, it is impossible to test the Onsager equation when applied to transference numbers in liquid ammonia.

Robinson and Stokes (66) have investigated the results of Jahn (67) on the transference numbers of the Cd^{++} ion in aqueous cadmium sulphate solution at 18°C. No moving-boundary data on di-divalent salts in water are available and Jahn's work involved the Hittorf method. However, Robinson and Stokes claim that over the concentration range 0 to 1 M the transference number of the Cd^{++} ion is found to fall almost linearly, within the limits of experimental error, on the t_+ vs. $\sqrt{c}$ plot. Using a small $\mathring{a}$ parameter of 3.5 Å. in the Onsager equation for transference numbers, together with the limiting ion conductances of Cd^{++} and $SO_4^=$ ions at 18°C. given by Deubner and Heise (68), good agreement between the calculated and observed values of t_+ was obtained.

It is well accepted that ion pairs form in solution, particularly in media of low dielectric constant, and with more highly charged species in water. The transference number is affected in a way in which there is an apparent 'dilution' of the solution by the removal of ions as ion pairs. The extent of this 'dilution' depends on the association constant K_A. Compensation for this effect by the use of the rather small $\mathring{a}$ parameter in the Onsager equation appears to account for the good agreement obtained. It will be of interest, therefore, when the relevant ion conductance data are available for liquid ammonia solutions, to compare the observed and

calculated transference numbers for uni-univalent salts. Nevertheless, a close similarity in this respect between uni-univalent salts in liquid ammonia and di-divalent salts in water does seen to be apparent.

Consideration of the Bjerrum 'critical distances' of closest approach emphasises the similarities between the two systems. Bjerrum (69) suggested as a simple approximation that the distance of closest approach of the ions in solution should be taken as the distance at which the mutual electrical potential energy of interaction, $z_+z_-e^2/\varepsilon q$, between the two ions is equated to the thermal energy, 2kT. Thus the 'critical distance',

$$q = \frac{z_+z_-e^2}{2kT\varepsilon},$$

represents the distance within which all ions must be regarded as existing as pairs. This is very much a crude approximation as there is no precise distance at which interaction starts and stops, and also, the ions are regarded as being point charges. The 'critical distance' provides a good qualitative means, however, of comparing ions in different solvents with different dielectric constants. If the dielectric constant of water is taken as 80, and that of liquid ammonia as 22, then the Bjerrum 'critical distances' for ion pairs in water and liquid ammonia at 25° and -33° respectively are shown in Table 11.

Table 11

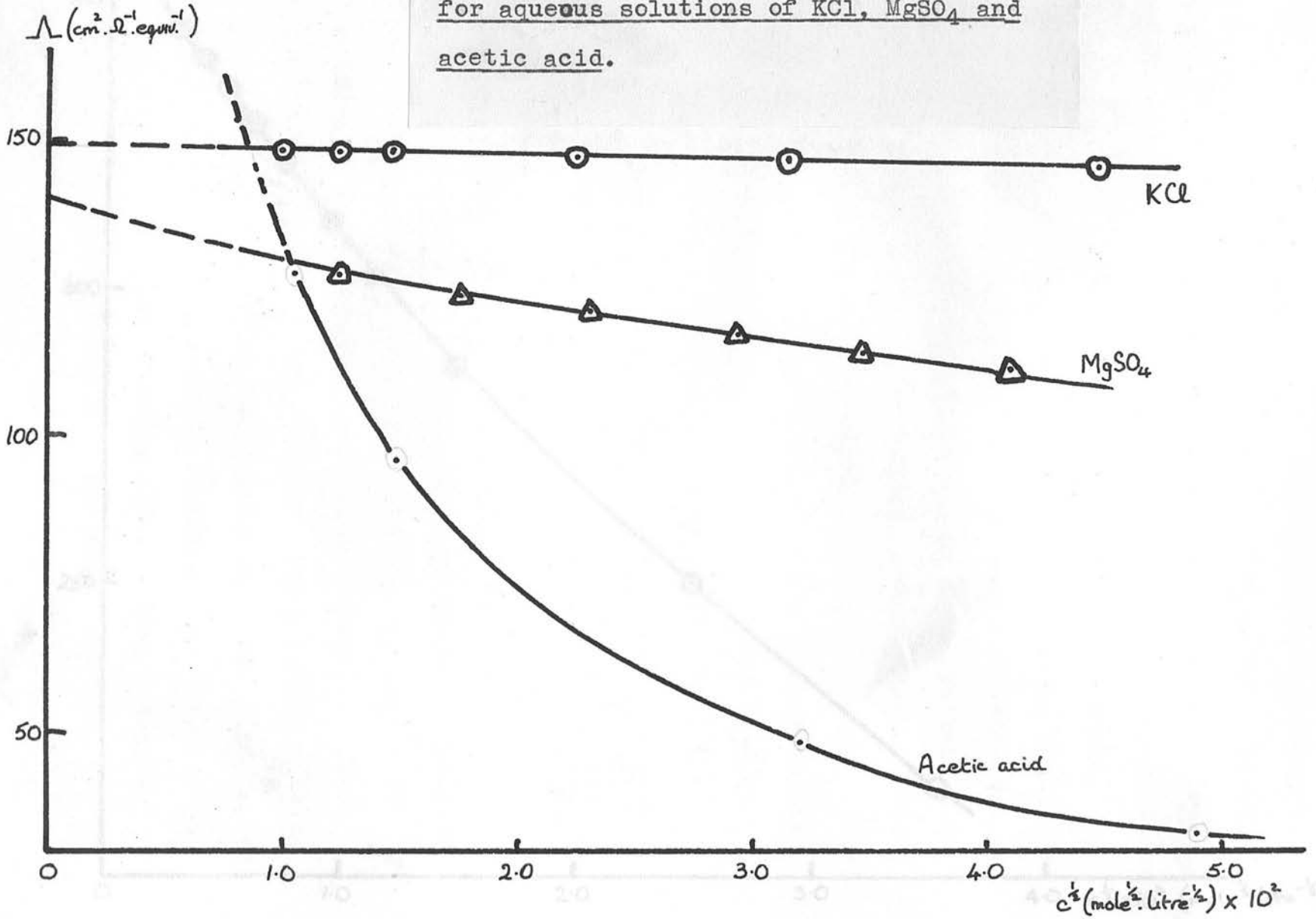
Bjerrum 'critical distances' in water and liquid ammonia.

Ion charge ratio	1:1	2:2	3:3
Water	3,5 Å.	14.0 Å.	31.5 Å.
Liquid ammonia	17.0 Å.	68.2 Å.	152.9 Å.

It is seen from Table 11 that the 'critical distances' for di-divalent salts in water and uni-univalent salts in liquid ammonia are comparable. Thus at a low concentration, of say 10^{-3} M, when the average separation of the ions is calculated to be 94 Å, there will be a significant proportion of ions which must be regarded as paired whatever distribution is considered. This number must be similar in the two systems.

Further/between the two systems is found by consideration of the conductance vs. concentration curves. Figure 8 shows the plots of conductance Λ vs. $\sqrt{c}$ for potassium chloride (41), magnesium sulphate (70) and acetic acid (71) in water. Figure 9 shows the Λ vs. $\sqrt{c}$ plot for potassium chloride in liquid ammonia taken from the data of Hnizda and Kraus (12). The qualitative similarity of the curves for magnesium sulphate in water and potassium chloride in liquid ammonia is obvious. Other uni-univalent salts in liquid ammonia have similar Λ vs. $\sqrt{c}$ plots, as can be seen from the data on alkali metal nitrates (9,10) and sodium and potassium bromides and potassium iodide (12), and sodium chloride (72,73). Similar curves are also obtained from the data of Gur'yanova and Pleskov (74) for the conductances of the 'strong' acids in

Figure 8. Graphs of the conductances, , against square roots of concentrations, , for aqueous solutions of KCl, $MgSO_4$ and acetic acid.



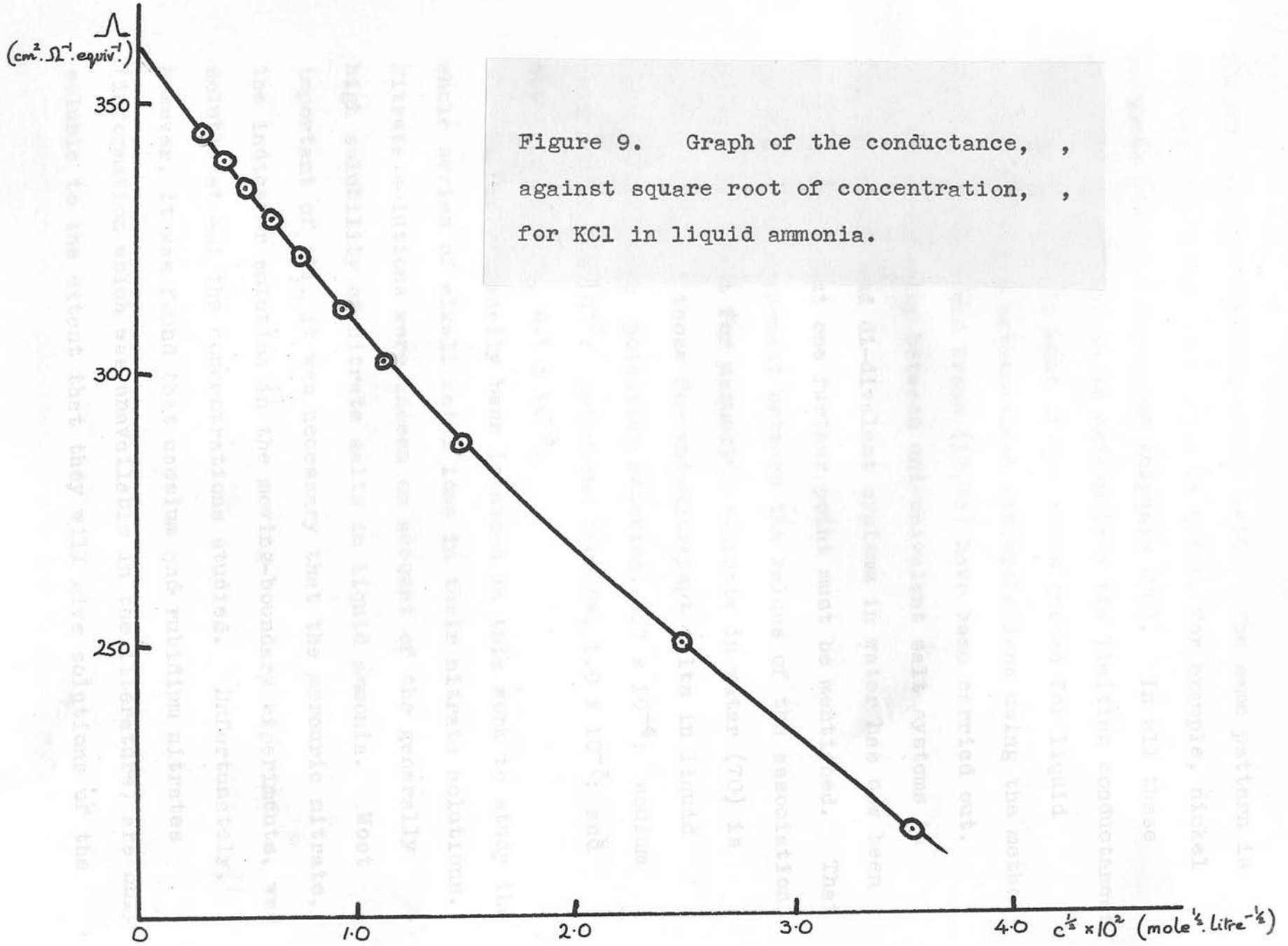


Figure 9. Graph of the conductance, , against square root of concentration, , for KCl in liquid ammonia.

liquid ammonia including acetic acid. The same pattern is followed by di-divalent salts in water, for example, nickel sulphate (75) and magnesium sulphate (70). In all these cases it is impossible to extrapolate the limiting conductances graphically, and in most of the cases quoted for liquid ammonia solutions mathematical extrapolations using the method devised by Fuoss and Kraus (13,76) have been carried out.

The similarity between uni-univalent salt systems in liquid ammonia and di-divalent systems in water has now been made apparent, but one further point must be mentioned. That is, the close agreement between the values of the association constants. That for magnesium sulphate in water (70) is 4.96×10^{-3}, and those for uni-univalent salts in liquid ammonia (12) are; potassium chloride, 8.7×10^{-4}; sodium chloride, 3.0×10^{-3}; potassium bromide, 1.9×10^{-3}; and potassium iodide, 4.1×10^{-3}.

It had originally been intended in this work to study the whole series of alkali metal ions in their nitrate solutions. Nitrate solutions were chosen on account of the generally high solubility of nitrate salts in liquid ammonia. Most important of all, it was necessary that the mercuric nitrate, the indicator solution in the moving-boundary experiments, was soluble at all the concentrations studied. Unfortunately, however, it was found that caesium and rubidium nitrates (information which was unavailable in the literature) are only soluble to the extent that they will give solutions of the

order of 10^{-2} M. At this concentration extrapolation of t_+ *vs.* $\sqrt{c}$ plots would have been impossible even if it had been possible to obtain values of t_+ for the individual concentrations. This situation was completely unexpected at the start of the work, as the other alkali nitrates have quite high solubilities.

It will be possible to circumvent this problem, for it has been established thatthe iodides of rubidium and caesium are sufficiently soluble for transference studies and, more important, that mercuric iodide, as the indicator solution, is soluble enough to give at least a 0.15 M solution. It will, however, be necessary to obtain the transference numbers of the K^+ ion in iodide solution as well as those of Cs^+ and Rb^+ ions. In this way they can be related to the existing values for nitrate solutions

A preliminary experiment (shown at the end of Appendix I) has already been performed with potassium iodide solution. In this experiment the boundary conditions were the clearest and sharpest found in any experiment so far. The conditions were so good that a precise determination of the transference numbers of the K^+ ion should be capable of improvement by improving the method by which the boundary is observed. It is hoped that this will provide a method for the establishment of a standard transference number measurement for use in liquid ammonia solutions. In the single experiment performed so far, very good internal consistency appears to exist within the

results. The transference number 0.4780 of the K^+ ion in 0.050 M KI solution at -55°C appears to be very similar to that of the nitrate ion at the same concentration and the same temperature, namely 0.4880. This implies similar conductances and mobilities for the nitrate and iodide ions. This is in reasonable agreement with the limiting conductances at -33°C obtained for KI, of 344.55 by Hnizda and Kraus (12) and for KNO_3 of 354 by Monoszan and Pleskov (9,10).

During this preliminary experiment on the electrolysis of the KI solution, it was observed that ~~potassium was liberated at~~ there appeared, at the platinum cathode, ~~This immediately re-dissolved to give~~ the intensely blue-coloured solution of the "solvated electron", ~~and~~ which after a short time had set up a sharp well-defined blue boundary which descended the cathode compartment at a steady rate. It would appear that an "autogenic" boundary of solvated electrons was being created and it will be interesting to design a cell for the measurement of the electron boundary together with the measurement of the transference number of the K^+ ion. Such a method might obviate the somewhat difficult operation of preparing solutions of known concentrations of alkali metals in liquid ammonia prior to the actual measurements of the transference number. In the single experiment performed the dimensions of the cathode compartment were not precisely known, but a very rough calculation showed that the electron boundary moved some seven to eight times as fast as the K^+ boundary. If the recent transference data of Dye, Sankauer and Smith (77) are compared, it is seen that the ion conductance of the Na^+ ion in a 0.05M sodium in ammonia

solution is about 42.5 and the electron conductance is 393 at -37°C. If the assumption is made that the conductance of the nitrate ion in 0.05M solutions of KNO_3 and $NaNO_3$ in liquid ammonia is independent of the cations, then, from the transference numbers found in this work for Na^+ and K^+ ions, the K^+ ion at -45°C should move 1.42 times as fast as the Na^+ ion. If this same ratio is taken to hold at -37°C then the ion conductance of the K^+ ion at that temperature should be about 59. Thus the "solvated" electron is expected to move some 6.7 times as fast as the K^+ ions. This would appear to be in reasonable agreement with the experiment, for it must be remembered that the boundary under observation is one of "solvated" electrons against a background of a 0.05M solution of KI.

During the electrolysis of solutions of $LiNO_3$, $NaNO_3$ and KNO_3 in liquid ammonia, a green fur-like deposit appeared on the cathode. In no case did this interfere with the course of the electrolysis. On stirring the contents of the transference cell at the end of an experiment it was found that this green deposit, when distributed throughout the cell, immediately appeared as a bright yellow solid with a very low solubility in ammonia. The explanation of the production of this material can only lie in deposition of alkali metal at the cathode, followed immediately by its solution to give the "solvated electron" solution thus;

$$K^+ + \varepsilon = K(metal).....cathode\ reaction$$

$$K(metal) + liq.NH_3 = K^+(NH_3)_x + \varepsilon(NH_3)_x$$

No electron boundaries were observed, except in the case of the electrolysis of KI solution, and no liberation of hydrogen occurred at the cathode, except in the case of the electrolysis of NH_4NO_3 solutions. In this last case there was no other visible reaction at the cathode. The volume of the green furry deposit appeared to be greater during the electrolysis of the $LiNO_3$ solutions and this was presumably a demonstration of the greater molar volume of lithium metal in ammonia solution than the other alkali metals.

A reduction reaction involving the solvated electron and nitrate ion must be postulated, and it is probable that the yellow compound previously obtained by Abe and Okabe (78-81) is produced at the cathode. These workers suggested a formula Na_2NO_2 and claim the substance to be explosive. Heslop and Robinson (82) describe a yellow compound of formula, Na_2NO_2, which is to be regarded as a sodium salt of nitroxylic acid, and quote its preparation by the electrolysis of sodium nitrite in liquid ammonia or by the reduction of sodium nitrite by a solution of sodium in ammonia. They do not mention any explosive characteristics, but claim the decomposition products to be N_2, Na_2O, $NaNO_2$ and $NaNO_3$ at 100°C. The compound is undoubtedly worthy of further investigation from the structural point of view but one further observation made in this work concerned its highly reducing properties. These were

demonstrated by removal of the solid as a slurry with a little liquid ammonia into the disposal flask, into which a large volume of water had been previously added. Much effervescence with evolution of hydrogen took place and the solid dissolved in the water to yield a colourless solution.

EXPERIMENTAL

The apparatus which was finally used for the determination of transference numbers was the result of several modifications of all the working parts. These modifications have not been described here and only the description of the final apparatus used is presented.

Descriptions of the various sections of the apparatus used are followed in this experimental section by a description of their use in a typical experiment. In the third part of this section the methods of calibration of the equipment are described followed by an account of how the moisture determinations and the preparative work were carried out. All the results obtained in the individual experiments have been collected together into Appendix I.

I. DESCRIPTION OF APPARATUS.

1. Transference cell. The transference cell, shown in Figure 10, consisted of a thin-walled precision-bore Pyrex glass tube A, of about 2.8 mm. internal diameter and 10 cm. long, graduated every 5 mm. Into the lower end of this tube was sealed a short length of tungsten wire B which entered the tube by about 3 mm. The tube A was graduated along its whole length at 5 mm. intervals in such a manner that there were 2 marks at each position so that each mark covered one quarter of the circumference of the tube. This

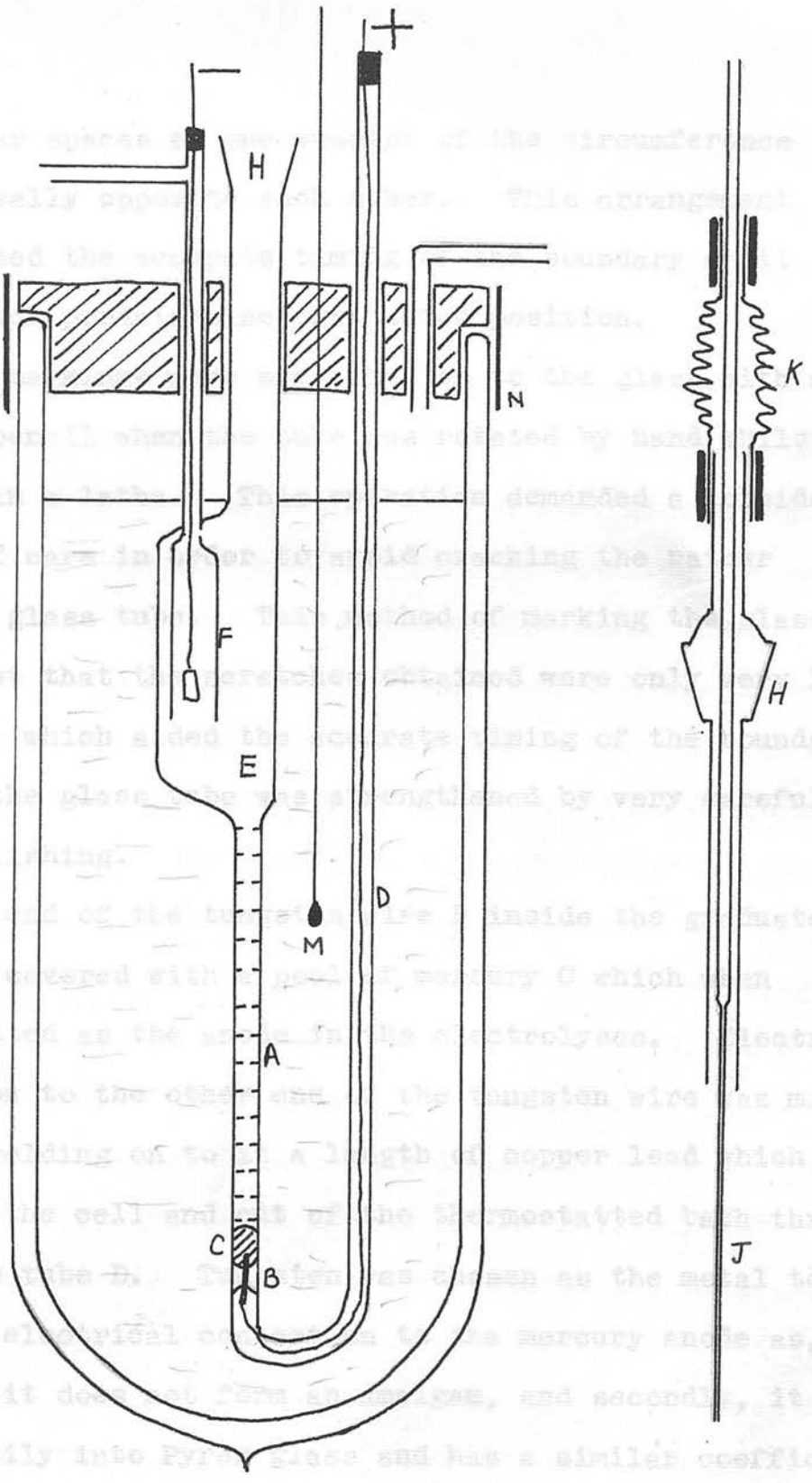


Figure 10. Transference cell and thermostatted bath.

left clear spaces of one quarter of the circumference diametrically opposite each other. This arrangement facilitated the accurate timing of the boundary as it passed each predetermined graduated position.

The markings were scratched on to the glass with a diamond pencil when the tube was rotated by hand whilst mounted in a lathe. This operation demanded a considerable amount of care in order to avoid cracking the rather delicate glass tube. This method of marking the glass also meant that the scratches obtained were only very light and fine, which aided the accurate timing of the boundary. Finally the glass tube was strengthened by very careful flame polishing.

The end of the tungsten wire B inside the graduated tube was covered with a pool of mercury C which when frozen acted as the anode in the electrolyses. Electrical connection to the other end of the tungsten wire was made by spot-welding on to it a length of copper lead which was led from the cell and out of the thermostatted bath through the glass tube D. Tungsten was chosen as the metal to make the electrical connection to the mercury anode as, firstly, it does not form an amalgam, and secondly, it seals easily into Pyrex glass and has a similar coefficient of expansion. An alternative method would have been to use platinum wire sealed through soda glass.

The graduated tube A opened into a wider compartment E

which contained, as the cathode compartment, a 3-cm. length of 1 cm.-diameter glass tube F. The platinum cathode was mounted on a stout platinum wire (S.W.G.18) which entered the cathode compartment through the gas inlet. This was brought out of the apparatus through a "pinch" seal in the glass which was backed with Picien wax just outside the thermostatted bath. A small hole was left at the top of the cathode but within the cell in order to equalise the pressure above the liquid in the two parts of the cell.

A ground glass B14 joint H which carried the delivery funnel J and its holder was mounted concentrically with the graduated tube A so that the thin delivery tube J could be slid in and out of the graduated tube to enable the delivery and removal of liquid. This device eliminated the formation of "air locks" in the graduated tube during the filling process and ensured the removal of all of the liquid after washing the cell. The delivery tube J was constructed from a thin-walled 2 mm.-bore glass tube drawn out so that it fitted as a funnel down the whole length of the delivery tube. A flexible vacuum-tight seal was made between the delivery tube J and its holder and guide by a rubber balloon K about 25 cm. long. This enabled the delivery tube to be withdrawn from and entered into the graduated tube without exposure of the contents of the cell to the atmosphere. The rubber balloon was held under sleeves made from rubber tubing which were wired firmly and well covered with silicone grease to help establish a good seal from the atmosphere. Great care was

taken not to allow any grease to get inside the apparatus and on to the delivery tube for it was found that with a little usage the grease would "creep" along the delivery tube. This caused drops of liquid ammonia solutions to be held on the delivery tube during the washing process and also during the experiments when it was withdrawn above the level of the liquid. These would have created uncertainties in the concentrations of the solutions being used which could not be tolerated.

2. Thermostatted bath. This consisted of an unsilvered Dewar flask, 10 cm. diameter and 30 cm. long, which contained liquid propane and a few boiling chips, shown in Figure 10. The Dewar flask was completely sealed by a large split cork through which the cell, a spirit thermometer M and the propane gas outlet tube were fitted. The cork which had been turned down to the shape shown in Figure 10 was completely covered with Picien wax and a rubber band N cut from a motor car inner-tube, about 6 cm. wide, was fitted over its edge and over the top few centimetres of the flask to make the whole vessel vacuum-tight.

Initially, several tests, under much more greatly reduced pressures than those required in the experiments, were made to establish the safety of the arrangement. After many trials lasting a few days in which the pressure was repeatedly reduced and then released, and without accident, it was considered that the apparatus could be used down to pressures of about 20 cm. Hg in complete safety. During these tests the flask was found to

be capable of holding a pressure of less than 1 mm. Hg for a prolonged period.

Constant temperatures, to better than ±0.1 C. degree could be maintained in the propane bath by controlling the pressure over the liquid propane to ±1 mm. Hg by the manostat arrangement. The temperatures of the bath were estimated to 0.1 C. degree with the spirit thermometer which had been previously calibrated against a thermocouple which was accurate to 0.05 C. degree.

3. Propane manostat. This consisted of the glass apparatus O, shown in Figure 11. The two limbs containing mercury were about 10 cm. in length and 4 cm. in diameter and were joined at the bottom through a capillary tube of 1.5 cm. internal diameter and at the top by a 7 cm. glass tube containing the stopcock a.

Gas pressures were controlled by causing the propane to flow through a sintered glass disc (porosity 1) mounted at the surface of the mercury.

To operate the system the vacuum pump was switched on with the stopcock a open and all others closed, until the required pressure showed on the manometer P. At this point tap a was closed so that a volume of gas was trapped in the closed limb of the vessel O. This trapped volume was at the required pressure when the mercury of the open limb was level with the sintered glass disc. If the pressure in the thermostatted bath fell then the mercury rose above the sinter, to prevent the

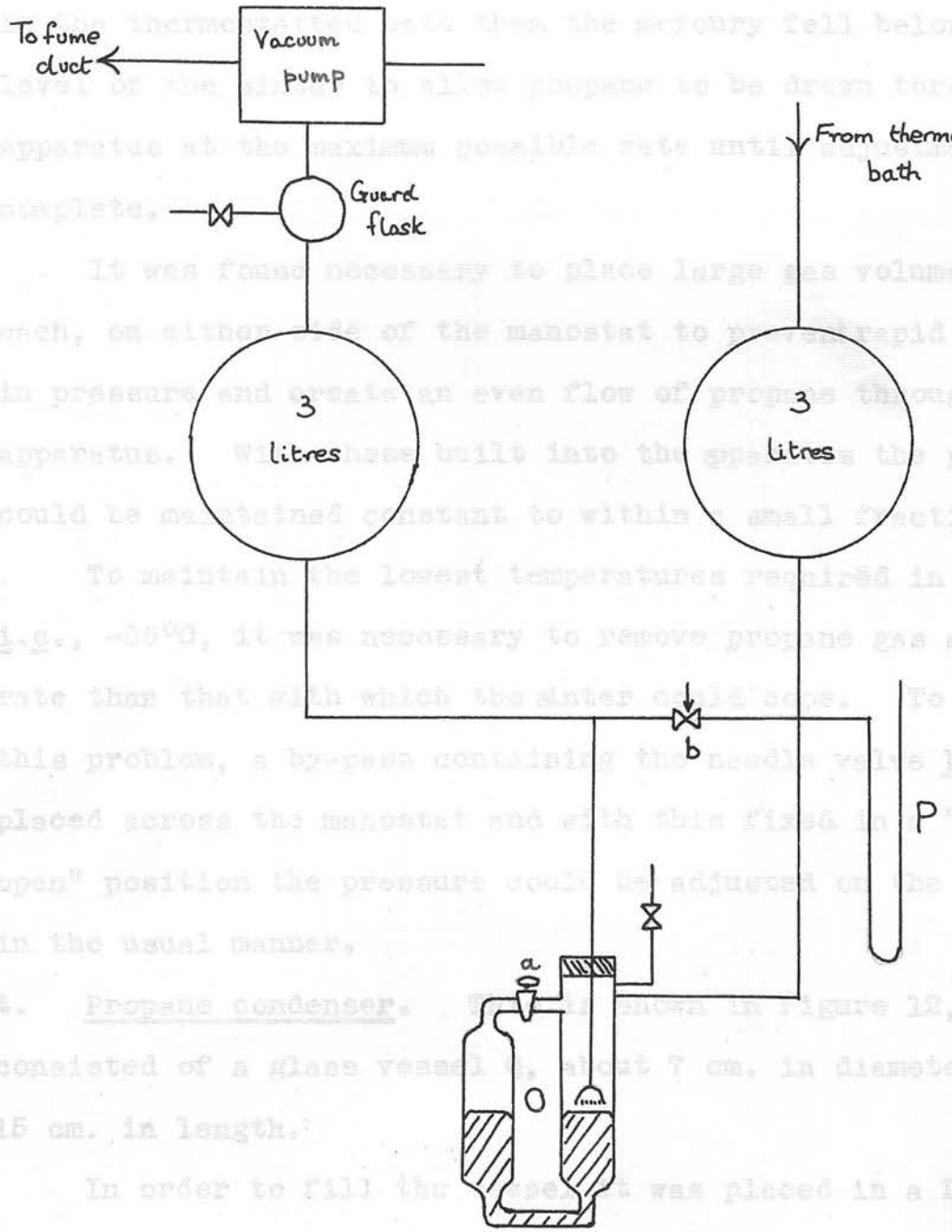


Figure 11. Propane manostat.

further flow of propane until the pressure rose again to the desired value. Alternatively, if the pressure rose too high in the thermostatted bath then the mercury fell below the level of the sinter to allow propane to be drawn through the apparatus at the maximum possible rate until adjustment was complete.

It was found necessary to place large gas volumes, 3 litres each, on either side of the manostat to prevent rapid oscillations in pressure and create an even flow of propane through the apparatus. With these built into the apparatus the pressures could be maintained constant to within a small fraction of a mm. Hg.

To maintain the lowest temperatures required in this work, i.e., -65°C, it was necessary to remove propane gas at a higher rate than that with which the sinter could cope. To overcome this problem, a by-pass containing the needle valve b was placed across the manostat and with this fixed in a "cracked open" position the pressure could be adjusted on the manostat in the usual manner.

4. Propane condenser. This is shown in Figure 12, and consisted of a glass vessel Q, about 7 cm. in diameter and 15 cm. in length.

In order to fill the vessel it was placed in a Dewar flask containing liquid nitrogen. Gaseous propane was passed in from the storage cylinder through the 7 mm. glass tube W. During the filling process a finger was placed lightly over the open end

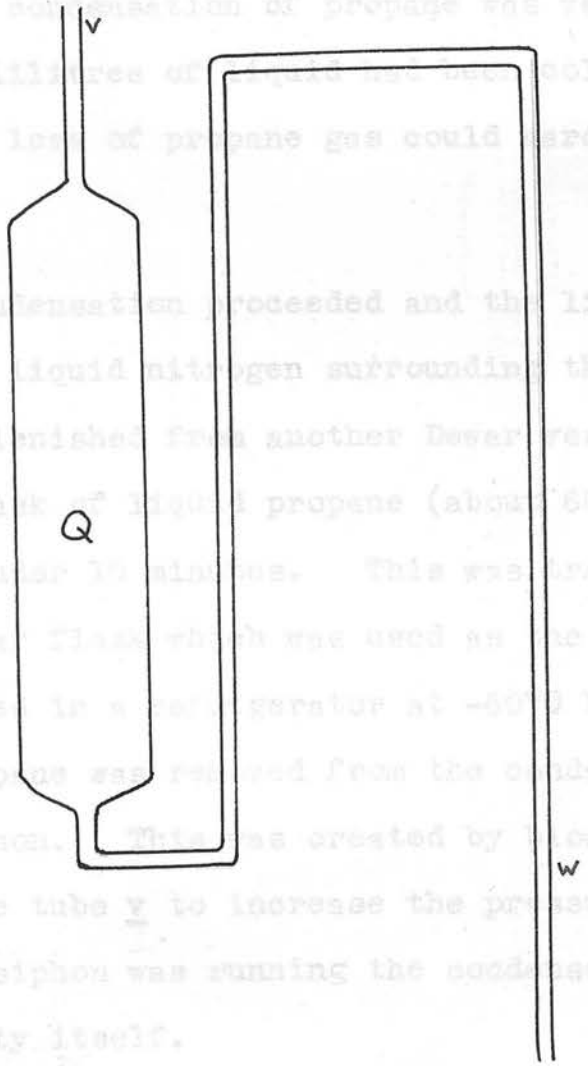


Figure 12. Propane condenser.

of the 7 mm.-bore glass tube v. This enabled a slight escape of propane from the tube v if the internal pressure of propane gas became excessive during the filling process and eliminated the risk of accidents from explosion. It was found that the condensation of propane was very efficient once a few millilitres of liquid had been collected in the vessel and the loss of propane gas could hardly be detected by smell.

As the condensation proceeded and the liquid nitrogen boiled off, the liquid nitrogen surrounding the condenser vessel was replenished from another Dewar vessel.

A full flask of liquid propane (about 600 ml.) could be collected in under 10 minutes. This was transferred to the unsilvered Dewar flask which was used as the thermostatted bath, and stored in a refrigerator at -60°C between experiments. The liquid propane was removed from the condenser flask by means of a siphon. This was created by blowing gently on the open end of the tube v to increase the pressure slightly in Q. When the siphon was running the condenser took about 45 seconds to empty itself.

5. Standard flask and disposal flask. These are illustrated together in Figure 13.

The standard flask R was fitted at its top with a B29 cone. Its volume was about 139 ml. and to facilitate accurate readings of volume it had a neck of about 1 cm. diameter which was graduated along its length (about 3 cm.) at 2 mm. intervals. The graduations were scratched on to the neck in the same manner

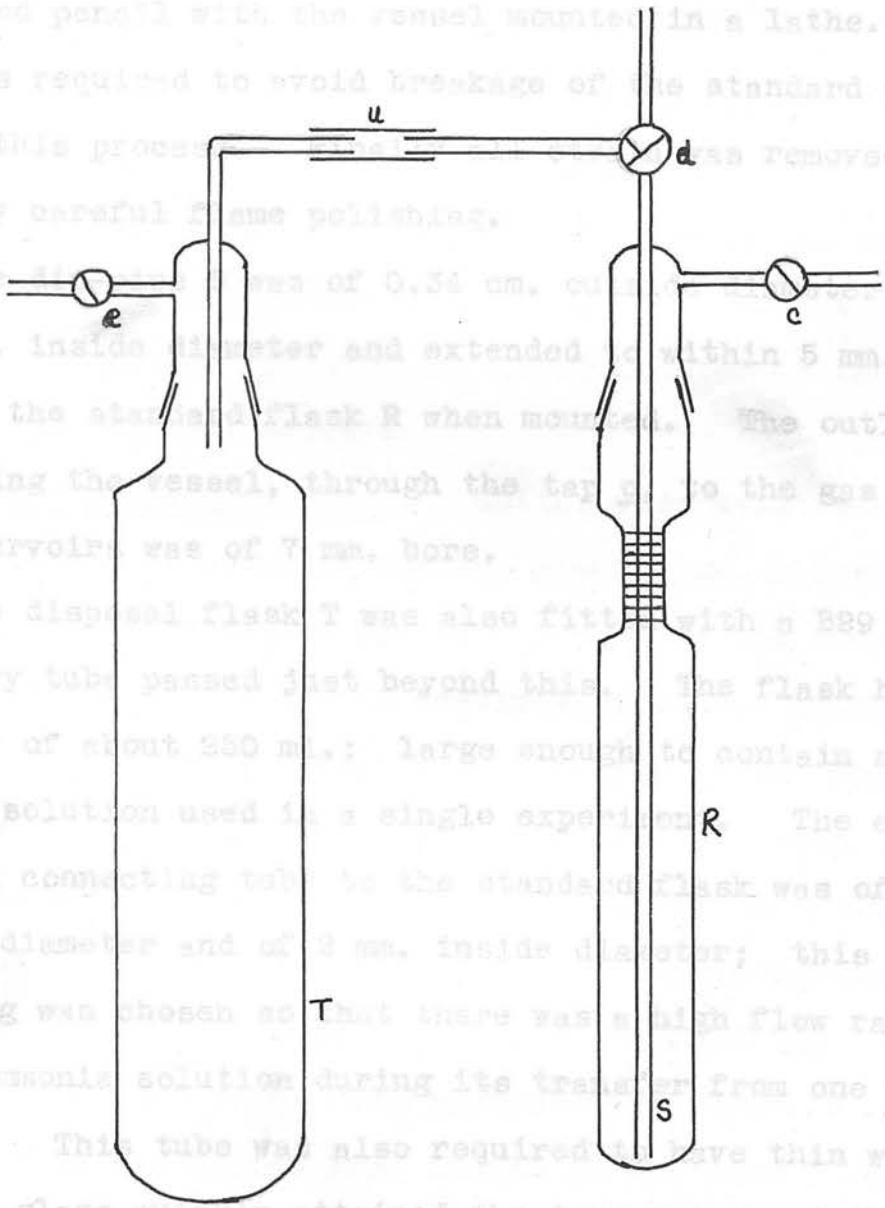


Figure 13. Standard flask and disposal flask arrangement.

as those on the calibrated tube of the transference cell, using a diamond pencil with the vessel mounted in a lathe. Great care was required to avoid breakage of the standard cell during this process. Finally all strain was removed from the glass by careful flame polishing.

The dip-pipe S was of 0.34 cm. outside diameter and of 0.18 cm. inside diameter and extended to within 5 mm. of the base of the standard flask R when mounted. The outlet tube connecting the vessel, through the tap c, to the gas lines and reservoirs was of 7 mm. bore.

The disposal flask T was also fitted with a B29 cone and the entry tube passed just beyond this. The flask had a capacity of about 250 ml.; large enough to contain all the ammonia solution used in a single experiment. The entry tube and connecting tube to the standard flask was of 3 mm. outside diameter and of 2 mm. inside diameter; this size of tubing was chosen so that there was a high flow rate of liquid ammonia solution during its transfer from one vessel to another. This tube was also required to have thin walls so that the glass quickly attained the temperature of the ammonia solution during the transfer, as this section of tubing did not possess a cold nitrogen "jacket" but was only lagged with cotton wool. Evaporation of the ammonia solutions passing along the tubing was thus kept at a minimum.

To prevent breakage of the delicate connecting tube between the standard flask R and the disposal flask T, some flexibility was given to the system by connecting the two ends of the tubes

from each flask with a short sleeve of tightly fitting polythene tubing u.

The disposal flask was connected with the gas lines and reservoirs with 7 mm.-bore tubing through the tap e.

The connection of both the standard flask and the disposal flask with the transference cell was made through a T-bore capillary stopcock, (d, of 2 mm.-bore) mounted in the liquid line between the two vessels.

6. Salt storage apparatus.. Solids were weighed by difference using a stoppered weighing bottle, about 1 cm. diameter and 5 cm. long, which fitted inside the B29 cone above the neck of the standard flask R. A "rough" estimation of the weight of a sample was obtained by weighing the sample in the weighing bottle on an Oertling single pan analytical balance. This gave the weight to the nearest 0.0001 g. The bottle containing the sample was then transferred to a Stanton micro-balance which was capable of weighing to the nearest 0.000002 g. Weights were thus recorded which were accurate to 0.00001 g.

While in use solids were stored in the tube V in the apparatus shown in Figure 14. The atmosphere in the apparatus was dried by phosphorus (V) oxide placed in the flask X. All joints were held firmly in place with springs.

To transfer solid to the weighing-bottle the cone W was quickly fitted into the ground glass socket of the weighing bottle and the solid was transferred by gentle shaking. The

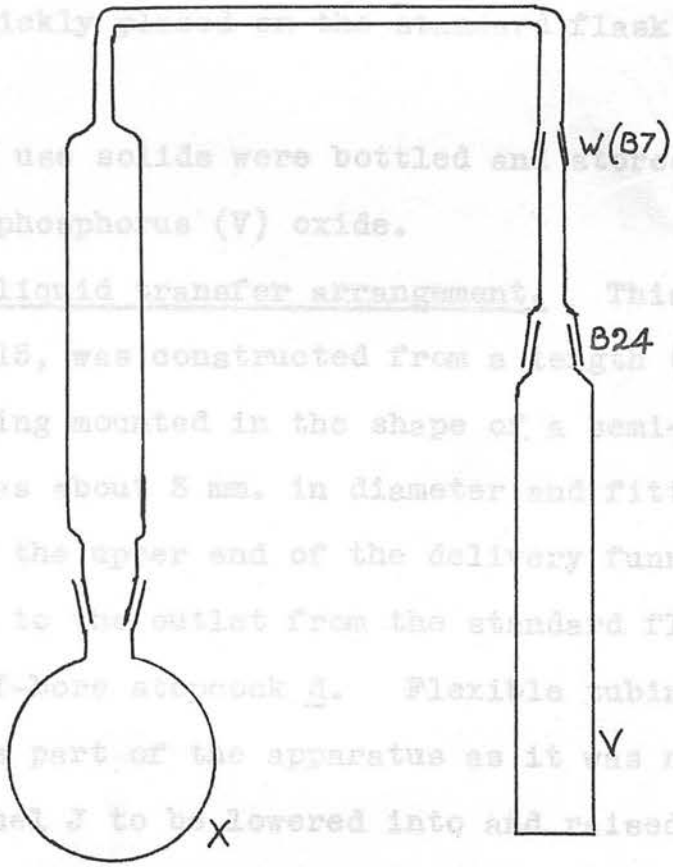


Figure 14. Salt storage apparatus.

stock sample and the weighing bottle top were then quickly replaced and the amount transferred was weighed out accurately. The weighed solid was then rapidly transferred to the standard flask R (the weighing bottle diameter being chosen to fit into the neck of the flask to effect this operation rapidly) and the stoppers were quickly placed on the standard flask and the weighing bottle.

When out of use solids were bottled and stored in a desiccator over phosphorus (V) oxide.

6. Siphon and liquid transfer arrangement. This arrangement, shown in Figure 15, was constructed from a length (about 60 cm.) of polythene tubing mounted in the shape of a semi-circle. The polythene tube was about 3 mm. in diameter and fitted tightly at one end on to the upper end of the delivery funnel J and at the other end on to the outlet from the standard flask R about 8 cm. above the T-bore stopcock d. Flexible tubing was required for this part of the apparatus as it was necessary for the delivery funnel J to be lowered into and raised from the solution in the transference cell. The thin-walled polythene tubing used was still flexible enough at -55°C to allow the required 15 cm. movement of the delivery funnel. At lower temperatures, however, the flexibility of the polythene was very greatly reduced, and it is this factor which, more than any other, placed the restriction on the temperatures at which solutions were to be prepared. If it had been possible to prepare and transfer solutions at lower temperatures than -55°C,

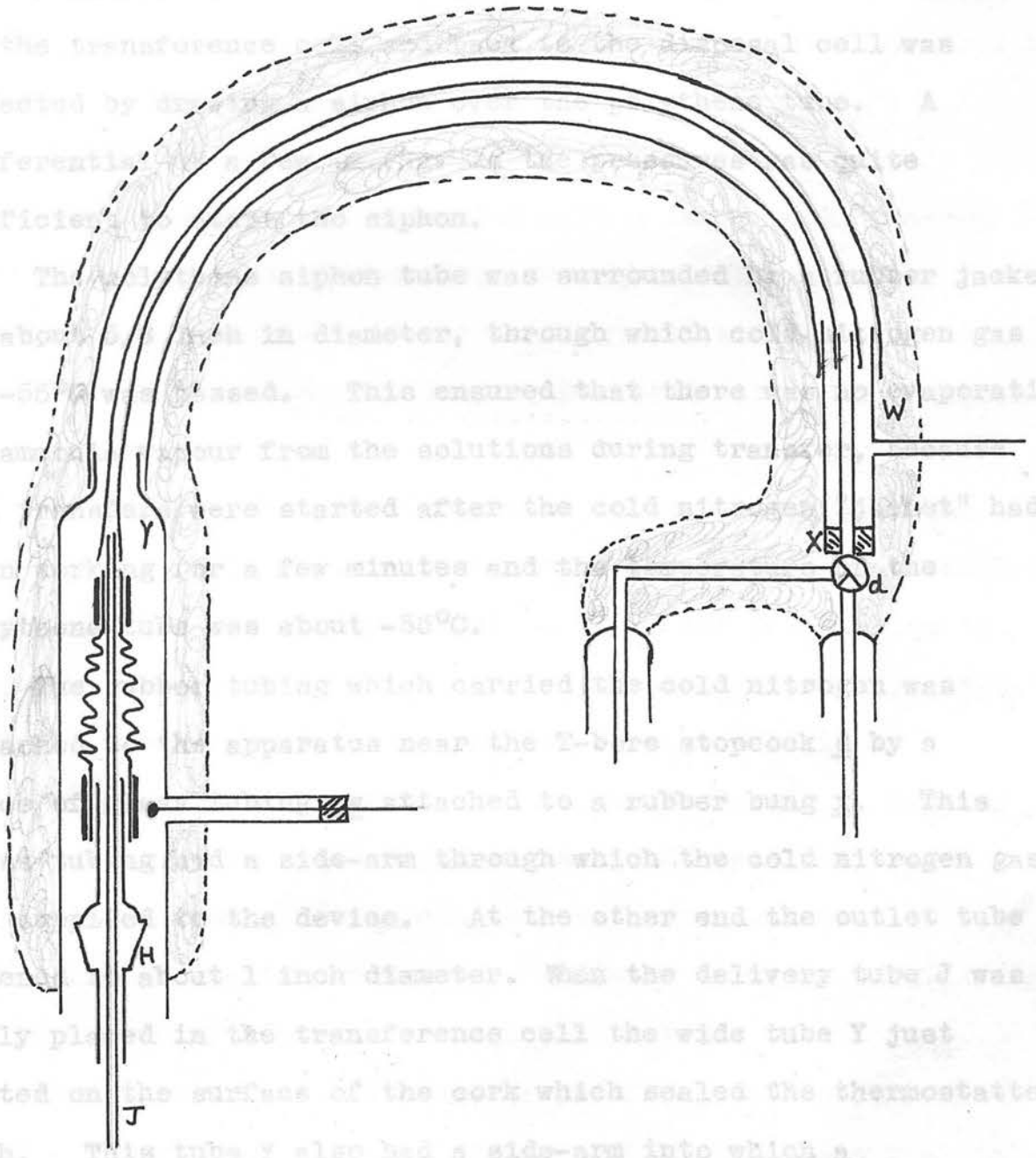


Figure 15. Liquid transfer line.

then errors due to the evaporation of ammonia vapour during transfer of solutions would have been greatly reduced.

Transfer of the ammonia solution from the standard flask to the transference cell and back to the disposal cell was effected by drawing a siphon over the polythene tube. A differential of a few mm. Hg. in the pressures was quite sufficient to start the siphon.

The polythene siphon tube was surrounded by a rubber jacket of about 5/8 inch in diameter, through which cold nitrogen gas at -55°C was passed. This ensured that there was no evaporation of ammonia vapour from the solutions during transfer, because all transfers were started after the cold nitrogen "jacket" had been working for a few minutes and the temperature of the polythene tube was about -55°C.

The rubber tubing which carried the cold nitrogen was attached to the apparatus near the T-bore stopcock d by a piece of glass tubing w attached to a rubber bung x. This glass tubing had a side-arm through which the cold nitrogen gas was supplied to the device. At the other end the outlet tube Y widened to about 1 inch diameter. When the delivery tube J was fully placed in the transference cell the wide tube Y just rested on the surface of the cork which sealed the thermostatted bath. This tube Y also had a side-arm into which a thermometer was fitted to aid the control of the temperature in the cold nitrogen "jacket" and which could also be used as a handle.

The outer covering of the jacketed line together with the connection between the disposal and standard flasks was well-lagged with a cotton wool covering about one inch thick. This was sealed and held firmly in position by wrapping the whole tightly with Sellotape.

The cold nitrogen gas supply, shown in Figure 16, consisted of a Dewar flask sealed with a large cork, covered with Picien wax and plastercine, through which passed the gas outlet tubes, the wires to the heating coil and an inlet funnel t. The wires to the heater coil were insulated with short lengths of glass tubing.

The outlet tubes were connected to the side-arm on the glass tube w, (Figure 15), by a length (about 20 cm.) of rubber tubing. This was left unlagged to allow the gas to rise in temperature to above -80°C before it passed into the "jacket". Care was needed not to allow the temperature to fall in the "jacket" and cause the ammonia solutions to freeze. Control of the temperature in the "jacket" was, however, not too difficult providing fairly constant attention was paid to it. Adjustment of the temperature was achieved by means of altering the flow rate of nitrogen through the system.

The nitrogen was generated by passing a current through the heater coil in the Dewar flask. This coil had a resistance of 37 ohms and to maintain a temperature of about -55°C in the "jacket" a potential difference of about 50 volts was required across the coil. Control was effected by supplying this voltage from a Variac transformer, fed from the A.C. mains.

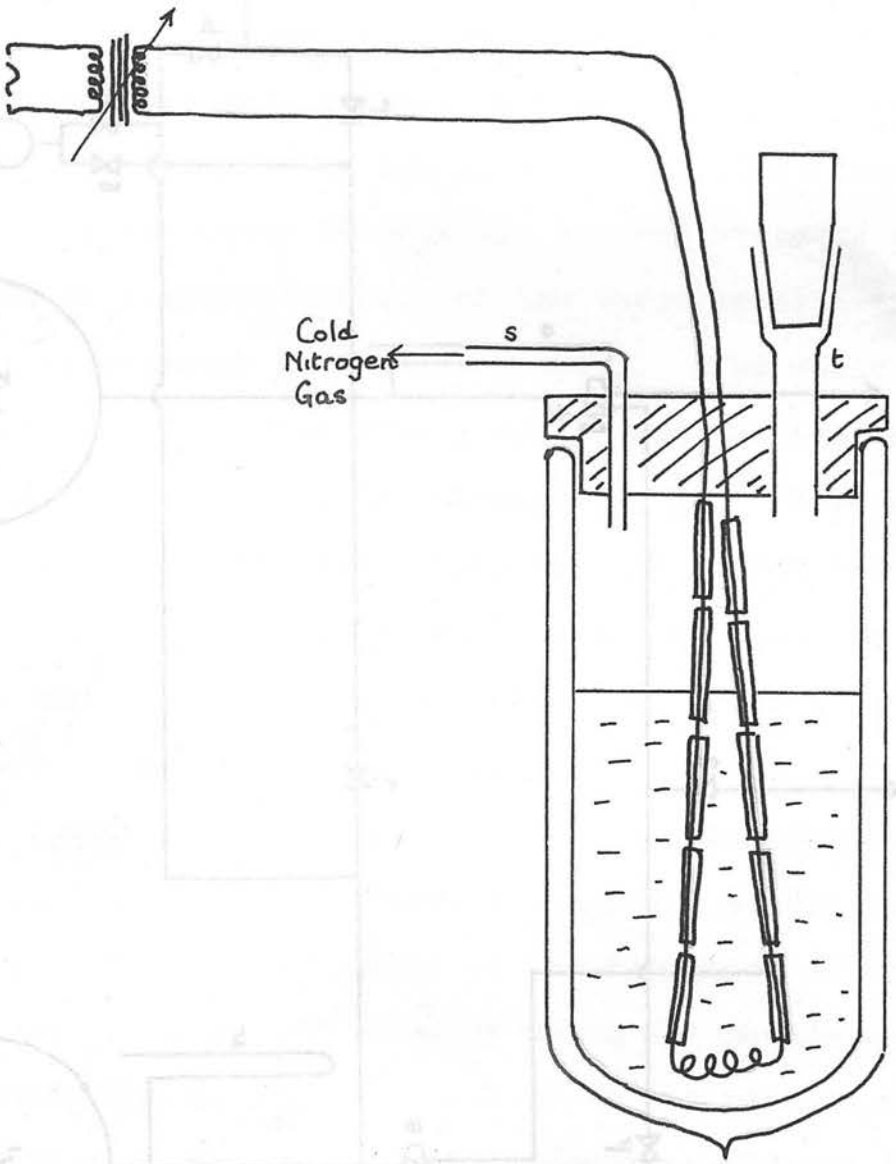


Figure 16. Cold nitrogen gas generator.

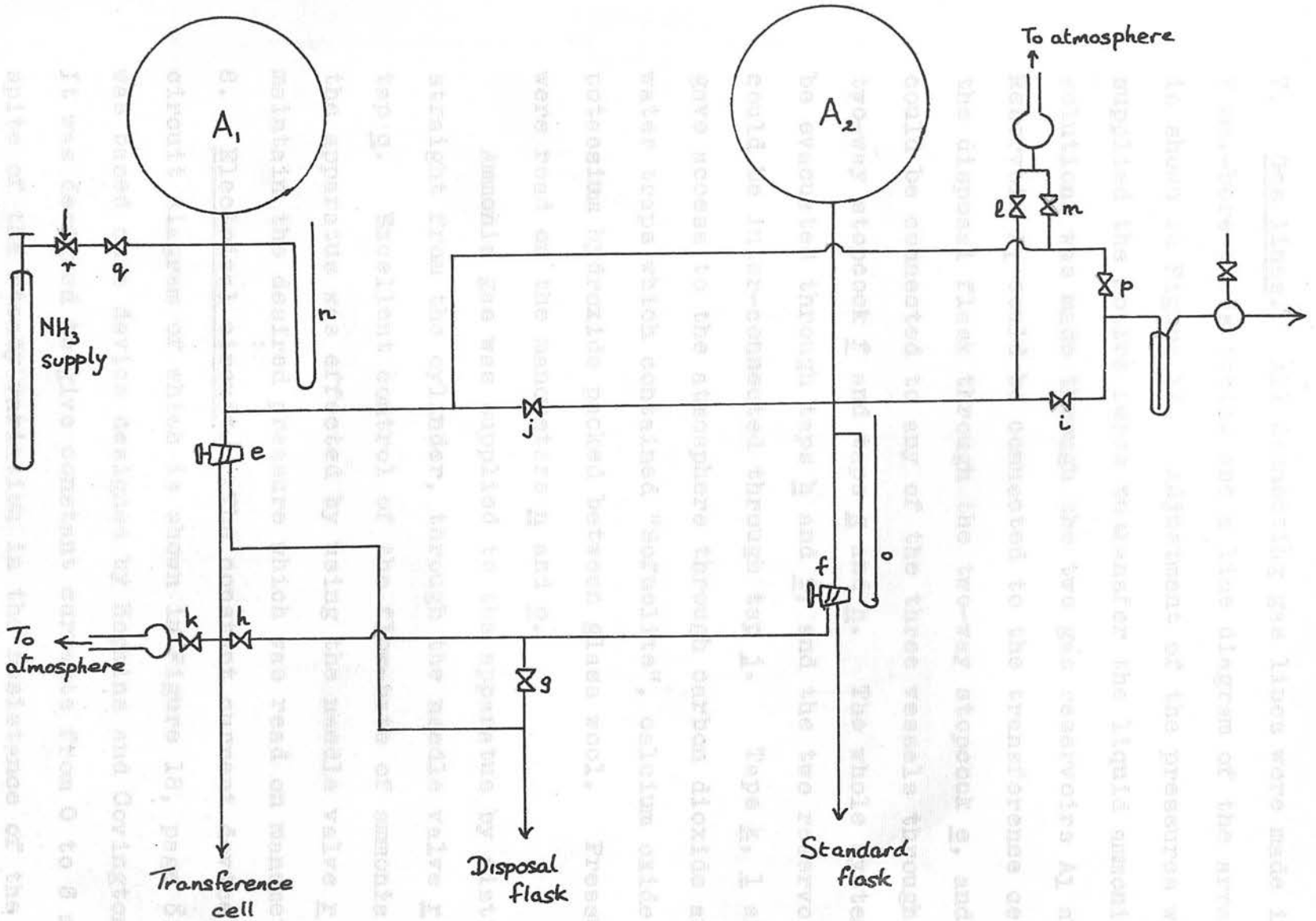


Figure 17. The gas lines.

7. Gas lines. All connecting gas lines were made in 7 mm.-bore glass tubing and a line diagram of the arrangement is shown in Figure 17. Adjustment of the pressures which supplied the motive force to transfer the liquid ammonia solutions was made through the two gas reservoirs A_1 and A_2. Reservoir A_1 could be connected to the transference cell or the disposal flask through the two-way stopcock e, and A_2 could be connected to any of the three vessels through the two-way stopcock f and taps g and h. The whole system could be evacuated through taps h and i, and the two reservoirs could be inter-connected through tap j. Taps k, l and m gave access to the atmosphere through carbon dioxide and water traps which contained "Sofnolite", calcium oxide and potassium hydroxide packed between glass wool. Pressures were read on the manometers n and o.

Ammonia gas was supplied to the apparatus by distillation straight from the cylinder, through the needle valve r and tap q. Excellent control of the flow-rate of ammonia gas into the apparatus was effected by using the needle valve r to maintain the desired pressure which was read on manometer n.

8. Electrical circuit. The constant current device, a circuit diagram of which is shown in Figure 18, page 82 was based on a device designed by Hopkins and Covington (83). It was designed to give constant currents from 0 to 3 mA in spite of the steady variation in the resistance of the

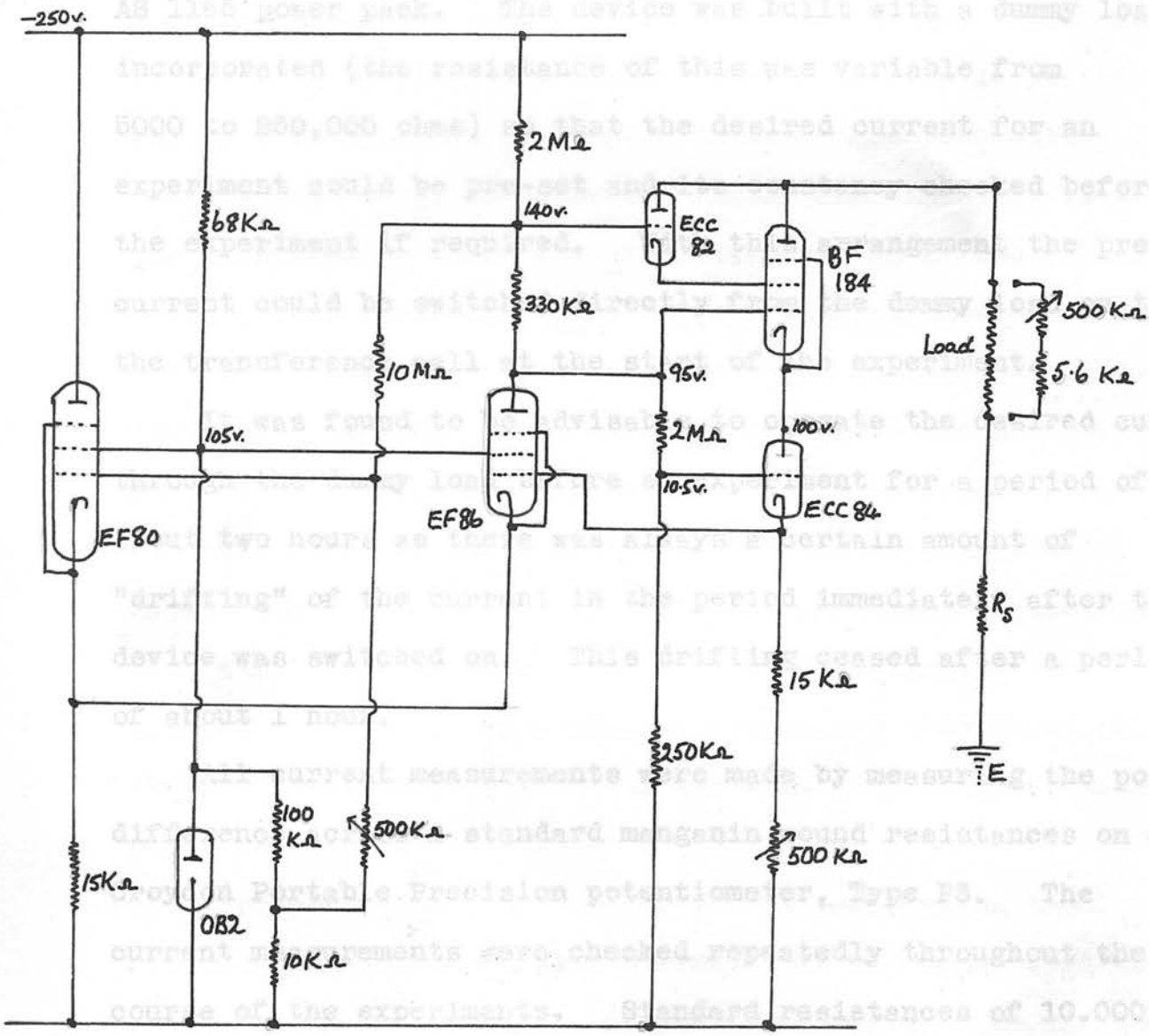


Figure 18. Constant current device.

transference cell during the experiments. The particular device which was constructed gave constant currents with any cell resistance from 5000 ohms to 250,000 ohms. It was supplied with a stable D.C. voltage of 650 volts from a Solartron AS 1165 power pack. The device was built with a dummy load incorporated (the resistance of this was variable from 5000 to 250,000 ohms) so that the desired current for an experiment could be pre-set and its constancy checked before the experiment if required. With this arrangement the pre-set current could be switched directly from the dummy load on to the transference cell at the start of the experiment.

It was found to be advisable to operate the desired current through the dummy load before an experiment for a period of about two hours as there was always a certain amount of "drifting" of the current in the period immediately after the device was switched on. This drifting ceased after a period of about 1 hour.

All current measurements were made by measuring the potential difference across a standard manganin wound resistances on a Croydon Portable Precision potentiometer, Type P3. The current measurements were checked repeatedly throughout the course of the experiments. Standard resistances of 10.000, 5.000 and 1.0016 ohms were included in the circuit for current measurement purposes.

II. USE OF THE APPARATUS.

In this section the use of the apparatus in the course of a typical experiment is described.

The first requirement before any experimental work started was that the apparatus should be scrupulously clean. This was achieved by washing with aqueous alcoholic caustic potash, followed by numerous washings with water and then allowing the transference cell, the disposal flask, and the standard flask and pipelines to stand for about two days in strong chromic acid. This was followed by copious washing with distilled water. Finally the apparatus was dried out by pumping it down under vacuum. This cleaning procedure was not carried out between every two experiments but was performed about once every two weeks although at no stage was any dirt or grease noticed in the apparatus. Between experiments copious washings with distilled water followed by completely drying the apparatus out by pumping down to vacuum was considered all that was necessary to maintain the apparatus in a satisfactorily clean condition.

1. Preparation of the solution. After pumping the apparatus down under vacuum overnight it was considered to be sufficiently dry to start another experiment. Pumping down was carried out with taps k, l and m and q closed, and h, g, j, i and p open, e open to the transference cell and f open to the standard flask R. To release the vacuum in the standard flask R

taps d (Figure 13), i and j were closed and l was cracked open to the atmosphere to allow air to enter very slowly through the guard tubes. This ensured that all water vapour and carbon dioxide was removed from the incoming air.

Tap f was nowclosed and the standard flask R, Figure 13, was quickly removed and fitted with a B29 stopper. The standard flask was designed with a cone joint above its neck in order to minimise contamination at this stage. The sample was weighed in the narrow weighing bottle and transferred very quickly into the standard flask, which was then replaced on the apparatus as quickly as possible. Exposure of the solid under test to the atmosphere could never have been more than a few seconds. Tap l was now closed and tap f opened and the apparatus was very slowly evacuated through i, taking great care not to disturb the solid in the bottom of the standard flask. A pressure of less than 1 mm. Hg was maintained for about 15 minutes before p and i were closed.

At this stage an unsilvered Dewar flask containing an acetone-solid carbon dioxide mixture at about -65°C was brought up around the standard flask. During the condensation of ammonia the temperature in this Dewar flask was maintained at about -65°C by the addition of small pieces of solid carbon dioxide.

Taps h and j were now closed and e (Figure 17) opened to the disposal flask; g was opened and the flow of ammonia was controlled with the needle valve r so that the pressure in the apparatus remained at about 1 cm. Hg below that of the atmosphere.

The tap d (Figure 13) was turned to connect the disposal flask and the standard flask so that ammonia gas passed down the dip-pipe and condensed on the surface of the vessel. A pool soon formed at the base of the vessel and dissolved all solid. When the liquid level rose above the end of the dip-pipe the bubbling of the ammonia into the liquid provided very good mixing which permitted good heat transfer across the walls of the vessel with a consequent rapid rate of condensation. The filling of the standard flask usually took about 20 - 30 minutes.

Liquid was condensed until the lowest graduation in the neck had been reached; at this point the taps d, r and q were closed and the temperature of the acetone-solid carbon dioxide bath was allowed to rise to -55°C. By dropping small pieces of solid carbon dioxide (about 1 ml. volume) every 30 seconds or so, it was possible to control the temperature in the Dewar flask to within 0.2 C. degree.

A Dewar flask containing acetone - solid carbon dioxide mixture at -55°C was now brought up around the disposal flask and tap h was closed when a small pool of liquid ammonia had condensed in the disposal flask. The two Dewar flasks were then maintained at -55°C for between half and one hour to allow the equilibration of temperatures throughout the liquid. During this time the tap c was opened together with j to connect the two gas reservoirs A_1 and A_2, and p and i to evacuate the gas system. When a suitable vacuum was reached (about 1 mm. Hg) the taps p and i were closed, q was opened and using the needle valve r, ammonia

was allowed to enter the gas reservoirs until the pressure on the manometer was the same as the saturated vapour pressure of ammonia at -55°C (table of saturated vapour pressures is given in Appendix VI). Finally, air was allowed to enter the system slowly through l or m through the guard tubes, until the apparatus was at atmospheric pressure.

After about 45 minutes, the taps e and f were opened to the disposal and standard flasks respectively, and finally tap d (Figure 13) was turned to connect the disposal flask with the standard flask and level the liquid in the latter. The liquid level was read in the neck of the standard flask and the taps, d, e and f were immediately closed. About four more similar readings of the volume of the solution were taken at about 5-minute intervals until constant volume readings were obtained and the concentration of the solution was calculated.

2. Transfer of the solution to the transference cell. The thermostatted bath, filled with liquid propane at about -55°C, was brought up around the transference cell, Figure 10, and connected to the propane manostat, Figure 11. The delivery funnel J was placed into the calibrated tube A of the cell and the current supply to the cold nitrogen generator, Figure 16, was switched on. (A setting of about 50 volts on the Variac transformer was found to give an average temperature of -55°C in the jacketed line). This was allowed to run for about 5 minutes before the transfer of the solution was started.

Tap j was closed to isolate A_1 from A_2 and the pressure in A_1 was reduced by about 1.5 cm. Hg by cracking open tap p. The two-way taps e and f were now opened to the transference cell and the standard flask respectively, and finally d (Figure 13) was opened to connect the transference cell with the standard flask through the siphon line. The flow rate of the liquid ammonia solution passing over the line was controlled by the tap d. When the cell had been filled, tap e was turned to connect the disposal flask with A_1; tap k was opened to bring the cell to atmospheric pressure and tap d was turned to connect the transference cell with the disposal flask. The cell now emptied itself automatically into the disposal flask but d was closed just before the last drop of solution entered the delivery tube. This prevented the formation of gas locks in the delivery line which could sometimes cause small bubbles to adhere to the walls of the calibrated tube of the cell.

This transference procedure was repeated a further twice and the fourth sample of solution which passed over into the cell was used as the test solution. During the final transfer of solution the pressure differential between A_1 and A_2 had usually fallen to a little less than 1 cm. Hg but this was still sufficient to form the siphon. After this final transfer the delivery tube was raised above the level of the liquid in the transference cell and its contents were carefully drawn back into the disposal flask. Taps e, h k and d were now closed, the supply of cold nitrogen was switched off and the main part of the experiment was ready to be started.

With experience the filling of the transference cell could be achieved in about 15 minutes from the time at which the concentration had been established.

3. The experiment. The pressure in the propane system was adjusted so that the boiling temperature of the propane was the temperature required in the experiment. Before the current was switched on to the transference cell, the cell and its contents were allowed to equilibrate in temperature for a period of about 45 minutes.

The constant current device, Figure 18, had been switched on at least two hours before this part of the experiment was due to start. When the cell temperatures had equilibrated the current, which had previously been set at about the required value, was switched from the dummy load to the transference cell.

In all experiments a clear sharp boundary appeared immediately. The solid mercury anode usually froze in the calibrated tube with an almost flat surface. This facilitated the formation of the boundary but in all cases when the mercury surface was irregular a clear sharp flat boundary had been set up before it had moved through one division (about 4 - 6 minutes). Observation of the boundary was aided by moving a slit of light vertically behind the tube against a white background. If this slit and the eye were aligned with the edges of the front and rear graduations, the time at which the boundary passed a calibration could be noted to within one second. The time at which the boundary seemed to disappear was taken as the time at which it passed the calibration mark.

In addition to noting the times at which the boundary passed the marks, the temperature of the thermostatted bath and the current supplied to the cell were recorded in order to check the constancy of these particular factors. A slight drift in temperature occurred in a few experiments and this was corrected by a slight adjustment of the propane pressure in the manostat.

The boundary was allowed to travel along the whole length of the calibrated tube, i.e., past all 18 marks and the current was previously set (immediately after the initial weighing of the sample had been carried out and the approximate concentration of solution was known) so that the duration of the experiment was greater than 4000 seconds. When the last mark had been passed the constant current supply was switched over to the dummy load and then to "off".

4. Removal of the solution. On completion of the experimental run the delivery tube was placed into the calibrated tube of the transference cell and the liquid ammonia solution was withdrawn to the disposal flask. Taps e and f (Figure 17) were opened to their respective vessels, the pressure was reduced in A_1 by a few cm. Hg, and the solution was allowed to flow from the transference cell to the disposal flask by opening tap d (Figure 13).

When all the ammonia solution had been removed from the transference cell the thermostatted bath was removed from the apparatus, stoppered and stored in the refrigerator at about -60°C.

The disposal flask was now removed from the apparatus and its

contents carefully poured into a large beaker placed in the sink of the fume cupboard. This was then cautiously filled with water. The disposal flask was washed with distilled water and replaced on the apparatus.

The standard flask was now removed, filled with distilled water and replaced. The transference cell and siphon line were washed with distilled water using the technique described in Section II.2. for the transfer of the solutions.

Finally all the washings in the disposal flask were discarded and the flask replaced. Tap d was turned to open all three ways and with g, k l and m closed and all other taps open, the system was evacuated until it was thoroughly dry.

III. CALIBRATIONS.

The two volumes which required calibration were the graduated tube of the transference cell and the volume of the standard flask. In both cases the volumes were determined at the ambient temperatures and corrections were made to the temperatures at which the apparatus was used.

1. The transference cell. The transference cell was mounted with its calibrated tube exactly vertical. This was achieved by clamping it firmly to the bench and arranging two cathetometer eye-pieces, previously adjusted to move vertically, at right angles to each other. The transference cell was adjusted until the traverses of both eye-pieces were exactly parallel to the calibrated tube. This was easily observed by focussing the cross-wires to run in line with the edge of the tube.

The room temperature was noted and the calibrated tube, after scrupulous cleaning, was filled with clean mercury so that the mercury meniscus was below the level of the top mark (Mark 1) by less than 0.01 cm. The cathetometer telescope was aligned so that it looked diagonally across the edges of the clear spaces and the marks, and so that both marks and the cathetometer eye-piece were horizontal. The reading was then noted for the top mark. The eye-piece was moved so that it was level with the top of the mercury meniscus and that reading was recorded.

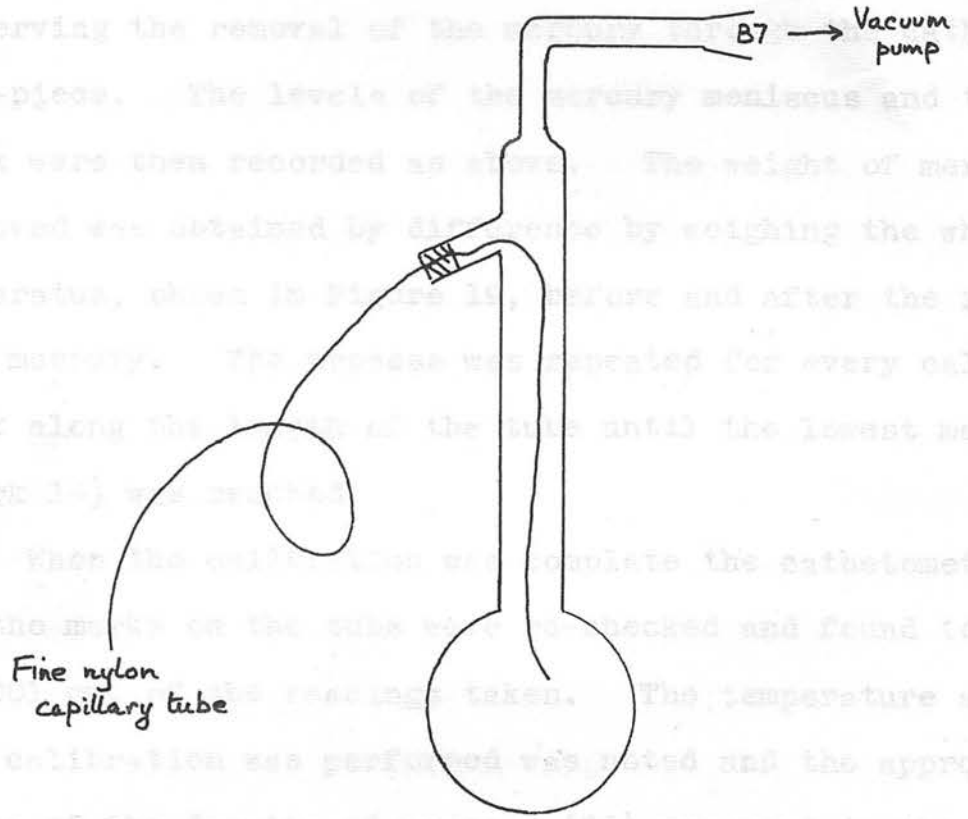


Figure 19. Calibrating device for transference cell.

Mercury was now removed from the calibrated tube by means of the device shown in Figure 19. The end of the fine nylon tube u (1 mm. in diameter) was placed on the surface of the mercury and the B7 joint was attached to a vacuum system and the pressure was reduced to about 40 cm. Hg. Mercury was carefully removed until the next mark (Mark 2) in the calibrated tube was just passed. This could easily be achieved by observing the removal of the mercury through the cathetometer eye-piece. The levels of the mercury meniscus and the nearest mark were then recorded as above. The weight of mercury removed was obtained by difference by weighing the whole apparatus, shown in Figure 19, before and after the removal of the mercury. The process was repeated for every calibration mark along the length of the tube until the lowest mark (Mark 18) was reached.

When the calibration was complete the cathetometer readings of the marks on the tube were re-checked and found to be within $\pm$0.001 cm. of the readings taken. The temperature at which the calibration was performed was noted and the appropriate value of the density of mercury (84) was used in the calculations.

Independent checks on the calibration were made by filling the tube with mercury to a particular mark, e.g., Mark 3, withdrawing mercury to another mark, e.g.,Mark 15, weighing the mercury, measuring the distances between the mercury menisci and the two marks, and comparing the result with the calibration

table. This procedure was carried out at intervals throughout the course of the work to check the constancy of the calibrations. It was established that, in spite of the many changes of temperature which the transference cell had to undergo, the calibration showed no detectable change in the course of the work.

A volume correction was calculated to allow for the temperature at which the apparatus was used. This amounted to 0.0008 ml. on a volume of 1 ml at -55°C. This correction was applied on the value of the transference number obtained. The same correction was applied regardless of the temperature of the experiment as the differences between the corrections over 10 C. degrees are negligible.

The results of the calibration are given in Appendix III. From these results a calibration chart was constructed from which the experimental results could be calculated (Appendix III); the minimum tube lengths included in this table were 4 cm.

2. Standard flask. This was first weighed empty, then filled to the lowest mark with boiled out distilled water and reweighed. The volumes between the graduations in the neck of the flask were determined by adding more water from a 1 ml. calibrated pipette. Using a micrometer-screwgauge the outside dimensions of the dip-pipe were recorded together with its length; the internal diameter was measured with the cathetometer.

From the above readings the volume of liquid which could be accommodated between the marks in the neck of the flask was

calculated. Finally the dip-pipe was placed in position and the rise in liquid level in the neck was noted to give the volume of glass in the dip-pipe.

The calibration, given in Appendix IV, was repeated three times during the course of the work but the differences in the volume found in each case were insignificant in spite of the large temperature changes which the flask had to undergo.

3. Standard resistances. These were measured potentiometrically, using a Vernier potentiometer and a digital voltmeter, by comparison against other known standard resistances. The values of the resistances used in the current determinations were 10.000, 5.000 and 1.0016 ohms. They were later measured on a Smith's Difference Bridge normally used in platinum resistance thermometry.

4. Time. The watch which was used in the experiments was checked daily against the radio time signals. It was always wound about six hours before the run was started, and always found to be correct to within 15 seconds in every 24 hours. This represents a very small error in the work and correction for time measurement was considered unnecessary.

IV. CALCULATION OF RESULTS.

Standard solutions were all prepared at -55°C but two thirds of the experiments were carried out at -45° and -65°C. The change in density of liquid ammonia is quite large over a 10 C. degree interval, e.g., 0.6961 g./ml. at -45°C and 0.7082 g./ml. at -55°C, and there is a correspondingly large change in molar concentration of the solutions.

Molar concentrations of the solutions were calculated at -45° and -65°C by assuming that the ratios of the densities of the solutions are the same as the ratios of the densities of pure liquid ammonia at the same temperatures. Thus a solution of concentration 0.1000 M at -55°C is

$$= 0.1000 \times \frac{0.7199}{0.7082}$$

$$= 0.1016 \text{ M at } -65^{\circ}\text{C, and}$$

$$= 0.1000 \times \frac{0.6961}{0.7082}$$

$$= 0.09835 \text{ M at } -45^{\circ}\text{C.}$$

The equation from which the transference numbers have been calculated

$$t_+ = \frac{V\ c\ F}{1000\ I\ T},$$

can be written as

$$t_+ = \frac{V}{T} \times K$$

where K is a constant for any one experiment, depending on the concentration and the current used. This constant was determined and used with each value of V (from Appendix III)

and T (recorded during the experiments). This allowed the calculation of a value of t_+ for every time recorded in the experiment. As only times greater than 2000 seconds were used this usually allowed 45 individual values of t_+ to be calculated. The arithmetic mean of these results was calculated and taken as the transference number at the particular concentration of the solution used in the experiment. The standard deviation from this mean was determined, and finally a correction to the transference number was made to allow for the difference in the volume of the apparatus at -55°C from the volume at the temperature of calibration.

The results are shown in Appendix I.

V. MOISTURE DETERMINATIONS.

1. Salts. It was important that all the salts and the liquid ammonia used should be perfectly dry. It was impracticable to attempt to estimate the water contents of the ammonium and lithium nitrates by heating at about 100°C, as both of these decompose slightly at such a temperature (85). Therefore, moisture determinations were carried out on all the salt samples by means of a Karl Fischer titration procedure.

The solid (about 2 g.) was placed in the titration cell, anhydrous methanol (15 ml.) was added and dry nitrogen gas (previously bubbled through Karl Fischer reagent) was bubbled through the slurry. The water present was determined from the quantity of Karl Fischer reagent required for the titration. The water content of the methanol was then determined by the addition of a further quantity of anhydrous methanol (15 ml.) followed by a further titration with Karl Fischer reagent. The subtraction of the second titre from the first gave the water content of the salt sample

The Karl Fischer reagent was standardised against a standard water solution in methanol.

Moisture contents of the salts were found to be:
NH_4NO_3, 0.04%; KNO_3, 0.02%; $NaNO_3$, 0.02%; $LiNO_3$, 0.05%.

2. Ammonia. The ammonia was very dry and to obtain a significant titration for its water content it was necessary to evaporate a considerable quantity of liquid ammonia. The technique adopted was similar to that developed by Hodgson

and Glover (86) in that a quantity of liquid ammonia was evaporated down from a mixture with ethylene glycol. Any residual ammonia was neutralised with glacial acetic acid (containing a little acetic anhydride to reduce the water content) and the mixture was titrated with Karl Fischer reagent. Blank titrations were performed on the ethylene glycol and the anhydrous acetic acid mixture.

Ammonia (about 135 ml.) was condensed in the usual manner in the standard flask (Experimental Section II.2). Anhydrous ethylene glycol (10 ml.) was placed in the disposal flask and the condensed ammonia was transferred to the disposal flask as described in the Experimental Section II.3. In this way the ammonia was being collected for its moisture determination in the same manner as in all the transference experiments.

Evaporation of the liquid ammonia was effected at a pressure of about 45 cm. Hg at room temperature. The reduced pressure was necessary for at atmospheric pressure the evaporation of ammonia, with its very high latent heat of evaporation, is a lengthy process. Even under these conditions evaporation took about four hours. To maintain a steady pressure the propane manostat was connected to the gas reservoir A_1.

When evaporation was complete dry acetic acid mixture (10 ml.) was added and the neutralised solution was quickly transferred to the titration cell. The solution was now titrated with Karl Fischer reagent and finally the mixture was run out of the titration cell. Ethylene glycol (10 ml.) and acetic acid mixture (10 ml.) were now added to the cell and a blank titration

was obtained for each of these solutions.

The results of one of the moisture determinations are described as follows:-

Volume of liquid ammonia condensed = 139 ml. at -55°C

Weight " " " " = 139 x 0.71

= 99 g.

Total water found in ammonia + 10 ml. glycol + 10 ml. acetic acid = 28.0 mg.

Water found in 10 ml. glycol = 3.7 mg.

Water " " 10 ml. acetic acid = 19.1 mg.

Therefore, water in 99 g. liquid ammonia

= 28.0 - (3.7 + 19.1)

= 5.2 mg.

Therefore, the liquid ammonia contains about 0.005% water.

It was evident that the moisture determination on the liquid ammonia was liable to very large errors, as the combined errors in the blank titrations on ethylene glycol and acetic acid would lead to about three times that error in the percentage water content. Thus, if there was an error of 2 mg. (10%) in the water content of the acetic acid and the ethylene glycol, there would be an error of 2 mg. in 5 mg. in the water content of the liquid ammonia. The determinations have, therefore, been regarded as possibly having an error of up to 100 per cent in the final figure obtained.

Other determinations gave water contents of 0.004% and 0.003% and the ammonia used in the work was regarded as having

a moisture content of less than 0.005% after one distillation from the storage cylinder.

3. Rate of moisture pick-up by ammonium nitrate. In order to assess the error due to the pick-up of moisture by the salts during handling, the following measurement of the rate of absorption of moisture by ammonium nitrate was made. A sample of the ammonium nitrate used in the transference measurements was tested. This salt was chosen on account of its very hygroscopic nature.

The ammonium nitrate (0.1280 g.) was thinly spread out on a small watch-glass and left on an Oertling single pan analytical balance with its front open to the atmosphere of the laboratory (relative humidity, 50%) at 20°C. The weight of the sample was recorded every few minutes as follows:-

Time(mins.)	Weight(g.)
0	0.1280
5	0.1285
7	0.1289
10	0.1291

The rate of moisture pick-up by ammonium nitrate on an open dish was thus shown to be relatively small. It was considered that during the short contact (less than 10 secs.) which the solid had with the atmosphere in the course of an experiment, and the fact that, at that time it was contained in a very narrow weighing-bottle, it was unlikely to take up a significant amount of water, especially as the relative humidity

was usually lower than at the time of this test.

VI. PREPARATIONS OF THE SALTS.

1. Ammonium, poassium and sodium nitrates. These were all of AnalaR grade. They were recrystallised three times from twice-distilled water. The wet crystals were placed in a vacuum desiccator over calcium chloride for about two days at atmospheric pressure. Fresh calcium chloride was added, and the pressure was reduced to vacuum for a further three days. Finally the salts were placed in a vacuum desiccator containing phosphorus (V) oxide and the pressure was reduced to a fraction of a mm. Hg for about one week.

When not in use the salts were stored in bottles with ground glass stoppers in a desiccator over phosphorus (V) oxide.

2. Lithium nitrate. An AnalaR grade of the salt was unobtainable and the technical grade was recrystallised five times from twice-distilled water.

Several attempts were made to dry this material satisfactorily. These usually resulted in the sample dissolving in its own water of crystallisation. For instance, one sample was dried in vacuum over calcium chloride overnight. The resulting, apparently dry, crystals when placed in a drying pistol and heated under vacuum to 61 °C, immediately dissolved in their own water of crystallisation. At this stage the crystals must have been mainly in the form of the hemi-hydrate $LiNO_3.\frac{1}{2}H_2O$.

Anhydrous lithium nitrate was eventually obtained by removal of the bulk of the water of crystallisation by drying in vacuum over calcium chloride for two to three days at room

temperature followed by drying over phosphorus (V) oxide for seven days at a pressure of 10^{-2} mm. Hg. During this time the crystals disintegrated into a fine dust indicating a change of crystal form involving the loss of the last molecule of water of crystallisation. Only at this stage, and not before, could the crystals be transferred to the drying pistol where they were heated for three weeks at 61°C (over boiling chloroform) over phosphorus (V) oxide at a pressure of 10^{-2} mm. Hg. When the lithium nitrate was removed it appeared as a fine dusty powder.

It was stored in a stoppered bottle in the same manner as the other salts.

3. Anhydrous methanol. The procedure adopted was that suggested by Evers and Knox (87).

Methyl alcohol (3 litres) was refluxed for 24 hours over magnesium turnings (35 g.). Care was taken during the initial heating stage as there was some hydrogen evolution with considerable effervescence; this subsided after about five minutes and the liquid refluxed gently.

The dry methyl alcohol (about 2.5 litres) was removed by distillation, in an apparatus fitted with moisture and carbon dioxide traps, into a flask containing AnalaR silver nitrate (15 g.). The alcohol was refluxed for a further 24 hours over the silver nitrate, a carbon dioxide and a moisture trap being fitted above the condenser. The solvent was next distilled twice, and the distillate (2 litres) was stored in

a well-stoppered dark glass bottle.

The purity was checked by measurement of the density; 0.7960 g./ml. at 15°C. This compares well with the value given by Timmermanns (88).

The water content, determined by Karl Fischer titration, was 0.04 mg./ml.

4. Anhydrous ethylene glycol. Smyth and Walls (89) dried ethylene glycol by repeated fractionation under vacuum. The middle fraction was then dried over anhydrous sodium sulphate.

In the present work ethylene glycol (500 ml.) was distilled at normal pressure and the fraction which boiled between 196° and 198°C was collected. The distillate (400 ml.) was refluxed with magnesium turnings (4 g.) for 24 hours. The ethylene glycol was then twice distilled in an apparatus guarded from moisture and carbon dioxide and the fraction distilling at 197°C was collected (about 250 ml.). The water content, by Karl Fischer titration, was 0.37 mg./ml. The density (1.1171 g./ml.) compared well with the figure of 1.11710 at 15°C given by Timmermans and Hennant-Roland (90).

5. Anhydrous acetic acid mixture. Glacial acetic acid was distilled in an apparatus guarded from moisture and the fraction distilling at 131°C was collected (250 ml). Acetic anhydride (0.5 ml.) was added to react with any remaining water. The mixture was refluxed for 12 hours and then anhydrous methanol (1 ml.) was added and the refluxing was continued for another

8 hours. Titrations with standard Karl Fischer reagent showed a moisture content of 1.8 to 2.0 mg. water per millilitre

APPENDIX I

The results of the experimental runs in this work have been collected together into this Appendix. The earlier experimental results, obtained while practice in the manipulation of the apparatus was being gained, and those from experiments in which there was some mishap due to failure in the apparatus or technique have been omitted.

The values of the transference numbers obtained from each experiment have been calculated as described in the Experimental Section IV, together with the standard deviations.

Finally, the values of the transference numbers which are used in the Results and Discussion Sections of this thesis have been obtained by making the correction for the change in volume of the transference cell between its temperature of calibration and the temperature of the experiment.

KNO_3 (0.11413 M at -48.0°C.) I = 3.090 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2281	0.4869	15 - 2	3698	0.4887
17 - 8	2564	0.4870	15 - 1	3984	0.4882
17 - 7	2847	0.4881	14 - 6	2274	0.4890
17 - 6	3132	0.4883	14 - 5	2557	0.4892
17 - 5	3415	0.4886	14 - 4	2943	0.4893
17 - 4	3701	0.4887	14 - 3	3129	0.4885
17 - 3	3987	0.4881	14 - 2	3413	0.4891
17 - 2	4271	0.4883	14 - 1	3698	0.4882
17 - 1	4556	0.4879	13 - 5	2277	0.4889
16 - 8	2278	0.4871	13 - 4	2563	0.4890
16 - 7	2561	0.4882	13 - 3	2849	0.4881
16 - 6	2846	0.4885	13 - 2	3133	0.4886
16 - 5	3129	0.4888	13 - 1	3418	0.4880
16 - 4	3415	0.4883	12 - 4	2277	0.4896
16 - 3	3701	0.4882	12 - 3	2563	0.4885
16 - 2	3985	0.4885	12 - 2	2849	0.4884
16 - 1	4270	0.4880	12 - 1	3132	0.4882
15 - 7	2274	0.4888	11 - 3	2277	0.4890
15 -6	2559	0.4890	11 - 2	2561	0.4893
15 - 5	2842	0.4893	11 - 1	2846	0.4886
15 - 4	3128	0.4893	10 - 2	2275	0.4897
15 - 3	2414	0.4885	10 - 1	2560	0.4890

$t_+(\text{ave.}) = 0.4886$, $\sigma = 0.0006$,

$t_+(\text{corr.}) = 0.4882$.

KNO_3 (0.06721 M at -48.0°C.) I = 1.658 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2522	0.4862	15 - 2	4102	0.4865
17 - 8	2836	0.4862	15 - 1	4418	0.4861
17 - 7	3148	0.4874	14 - 6	2520	0.4872
17 - 6	3465	0.4874	14 - 5	2838	0.4868
17 - 5	3783	0.4870	14 - 4	3155	0.4869
17 - 4	4100	0.4871	14 - 3	3471	0.4862
17 - 3	4416	0.4866	14 - 2	3787	0.4867
17 - 2	4732	0.4866	14 - 1	4103	0.4860
17 - 1	5048	0.4863	13 - 5	2523	0.4872
16 - 8	2522	0.4858	13 - 4	2840	0.4872
16 - 7	2834	0.4872	13 - 3	3156	0.4868
16 - 6	3151	0.4871	13 - 2	3472	0.4868
16 - 5	3469	0.4868	13 - 1	3788	0.4861
16 - 4	3786	0.4869	12 - 4	2525	0.4874
16 - 3	4102	0.4864	12 - 3	2841	0.4866
16 - 2	4418	0.4865	12 - 2	3157	0.4867
16 - 1	4734	0.4861	12 - 1	3473	0.4862
15 - 7	2517	0.4876	11 - 3	2526	0.4868
15 - 6	2834	0.4875	11 - 2	2842	0.4868
15 - 5	3152	0.4871	11 - 1	3158	0.4863
15 - 4	3469	0.4872	10 - 2	2525	0.4872
15 - 3	3785	0.4866	10 - 1	2841	0.4866

t_+(ave.) = 0.4868, σ = 0.0004,

t_+(corr.)= 0.4864.

KNO_3 (0.060919 M at -48.0°C.) I = 1.5655 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2403	0.4896	15 - 2	3908	0.4871
17 - 8	2703	0.4867	15 - 1	4210	0.4867
17 - 7	3003	0.4875	14 - 6	2405	0.4871
17 - 6	3304	0.4877	14 - 5	2706	0.4871
17 - 5	3605	0.4875	14 - 4	3007	0.4873
17 - 4	3906	0.4878	14 - 3	3309	0.4866
17 - 3	4208	0.4872	14 - 2	3610	0.4872
17 - 2	4509	0.4872	14 - 1	3912	0.4865
17 - 1	4811	0.4868	13 - 5	2405	0.4876
16 - 8	2402	0.4867	13 - 4	2706	0.4879
16 - 7	2702	0.4875	13 - 3	3008	0.4870
16 - 6	3003	0.4877	13 - 2	3309	0.4874
16 - 5	3304	0.4876	13 - 1	3611	0.4866
16 - 4	3605	0.4878	12 - 4	2407	0.4879
16 - 3	3907	0.4871	12 - 3	2709	0.4869
16 - 2	4208	0.4873	12 - 2	3010	0.4871
16 - 1	4510	0.4868	12 - 1	3312	0.4864
15 - 7	2402	0.4875	11 - 3	2406	0.4876
15 - 6	2703	0.4877	11 - 2	2708	0.4875
15 - 5	3004	0.4876	11 - 1	3010	0.4868
15 - 4	3305	0.4879	10 - 2	2407	0.4877
15 - 3	3607	0.4872	10 - 1	2709	0.4869

t_+(ave.) = 0.4872, σ = 0.0004,

t_+(corr.)= 0.4868.

KNO_3 (0.028392 M at -48.0°C.) I = 0.7453 mA.

Marks	Time	t_+	Marks	Time	t_+
16 - 8	2357	0.4855	14 - 6	2362	0.4855
16 - 7	2655	0.4857	14 - 5	2658	0.4854
16 - 6	2950	0.4860	14 - 4	2956	0.4853
16 - 5	3246	0 4859	14 - 3	3254	0.4844
16 - 4	3544	0.4858	14 - 2	3552	0.4847
16 - 3	3842	0.4850	13 - 5	2364	0.4857
16 - 2	4140	0.4849	13 - 4	2662	0.4856
15 - 7	2361	0.4855	13 - 3	2960	0.4845
15 - 6	2656	0.4859	13 - 2	3258	0.4855
15 - 5	2952	0.4858	12 - 4	2368	0.4855
15 - 4	3250	0.4857	12 - 3	2666	0.4844
15 - 3	3548	0.4848	12 - 2	2964	0.4842
15 - 2	3846	0.4846	11 - 3	2372	0.4842
10 - 2	2372	0.4845	11 - 2	2670	0.4841

t_+(ave.) = 0.4851, σ = 0.0006,

t_+(corr.)= 0.4847.

KNO_3 (0.012101 M at -48.0°C.) I = 0.3381 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 8	2513	0.4815	15 - 3	3349	0.4826
17 - 7	2788	0.4830	15 - 2	3627	0.4828
17 - 6	3067	0.4832	15 - 1	3904	0.4828
17 - 5	3344	0.4835	14 - 5	2514	0.4824
17 - 4	3624	0.4836	14 - 4	2794	0.4825
17 - 3	3901	0.4834	14 - 3	3071	0.4823
17 - 2	4179	0.4836	14 - 2	3349	0.4830
17 - 1	4456	0.4834	14 - 1	3626	0.4825
16 - 7	2510	0.4827	13 - 4	2516	0.4827
16 - 6	2789	0.4830	13 - 3	2793	0.4825
16 - 5	3066	0.4834	13 - 2	3071	0.4830
16 - 4	3346	0.4835	13 - 1	3348	0.4827
16 - 3	3623	0.4832	12 - 3	2516	0.4822
16 - 2	3901	0.4835	12 - 2	2794	0.4826
16 - 1	4178	0.4833	12 - 1	3071	0.4825
15 - 6	2515	0.4821	11 - 2	2516	0.4826
15 - 5	2792	0.4836	11 - 1	2793	0.4825
15 - 4	3072	0.4828	10 - 1	2517	0.4820

t_+(ave.) = 0.4829, σ = 0.0004,

t_+(corr.)= 0.4825.

KNO_3 (0.10761 M at -55.0°C.) I = 2.806 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2354	0.4898	15 - 2	3820	0.4912
17 - 8	2647	0.4899	15 - 1	4114	0.4909
17 - 7	2941	0.4906	14 - 6	2350	0.4913
17 - 6	3235	0.4909	14 - 5	2645	0.4911
17 - 5	3530	0.4908	14 - 4	2938	0.4916
17 - 4	3823	0.4912	14 - 3	3231	0.4911
17 - 3	4116	0.4909	14 - 2	3525	0.4917
17 - 2	4411	0.4909	14 - 1	3819	0.4909
17 - 1	4705	0.4906	13 - 5	2350	0.4918
16 -8	2353	0.4895	13 - 4	2645	0.4920
16 - 7	2647	0.4905	13 - 3	2937	0.4916
16 - 6	2941	0.4908	13 - 2	3230	0.4920
16 - 5	3236	0.4907	13 - 1	3524	0.4914
16 - 4	3529	0.4912	12 - 4	2352	0.4920
16 - 3	3822	0.4908	12 - 3	2643	0.4918
16 - 2	4116	0.4910	12 - 2	2936	0.4921
16 - 1	4410	0.4906	12 - 1	3229	0.4917
15 - 7	2351	0.4909	11 - 3	2351	0.4917
15 - 6	2645	0.4912	11 - 2	2645	0.4919
15 - 5	2940	0.4911	11 - 1	2937	0.4916
15 - 4	3233	0.4916	10 - 2	2351	0.4920
15 - 3	3526	0.4911	10 - 1	2643	0.4917

t_+(ave.) = 0.4912, σ = 0.0006,

t_+(corr.)= 0.4907.

KNO_3 (0.071899 M at -55.0°C.) I = 2.001 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2210	0.4888	15 - 4	3038	0.4901
17 - 8	2485	0.4889	15 - 3	3315	0.4894
17 - 7	2761	0.4896	15 - 2	3592	0.4893
17 - 6	3038	0.4897	14 - 6	2210	0.4894
17 - 5	3315	0.4896	14 - 5	2487	0.4893
17 - 4	3592	0.4898	14 - 4	2764	0.4896
17 - 3	3869	0.4893	14 - 3	3040	0.4891
17 - 2	4146	0.4893	14 - 2	3318	0.4894
16 - 8	2209	0.4886	13 - 5	2211	0.4898
16 - 7	2485	0.4895	13 - 4	2488	0.4900
16 - 6	2762	0.4896	13 - 3	2765	0.4892
16 - 5	3039	0.4895	13 - 2	3042	0.4895
16 - 4	3316	0.4897	12 - 4	2212	0.4902
16 - 3	3593	0.4891	12 - 3	2489	0.4893
16 - 2	3870	0.4893	12 - 2	2766	0.4894
15 - 7	2209	0.4895	11 - 3	2212	0.4897
15 - 6	2484	0.4899	11 - 2	2489	0.4897
15 - 5	2759	0.4902	10 - 2	2214	0.4895

t_+(ave.) = 0.4895, σ = 0.0003

t_+(corr.)= 0.4891.

KNO_3 (0.042031 M at -55.0°C.) I = 1.0524 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2463	0.4875	15 - 2	4003	0.4881
17 - 8	2770	0.4875	15 - 1	4310	0.4880
17 - 7	3075	0.4886	14 - 6	3466	0.4875
17 - 6	3383	0.4888	14 - 5	2774	0.4876
17 - 5	3691	0.4888	14 - 4	3081	0.4882
17 - 4	3998	0.4891	14 - 3	3390	0.4875
17 - 3	4307	0.4885	14 - 2	3696	0.4884
17 - 2	4613	0.4888	14 - 1	4003	0.4877
17 - 1	4920	0.4885	13 - 5	2468	0.4877
16 - 8	2466	0.4875	13 - 4	2775	0.4883
16 - 7	2771	0.4879	13 - 3	3084	0.4875
16 - 6	3079	0.4882	13 - 2	3390	0.4883
16 - 5	3387	0.4883	13 - 1	3697	0.4878
16 - 4	3694	0.4887	12 - 4	2469	0.4882
16 - 3	4004	0.4879	12 - 3	2768	0.4891
16 - 2	4309	0.4885	12 - 2	3084	0.4879
16 - 1	4616	0.4881	12 - 1	3391	0.4876
15 - 7	2465	0.4876	11 - 3	2471	0.4875
15 - 6	2773	0.4879	11 - 2	2777	0.4879
15 - 5	3081	0.4880	11 - 1	3084	0.4876
15 - 4	3388	0.4885	10 - 2	2469	0.4880
15 - 3	3697	0.4878	10 - 1	2976	0.4876

t_+(ave.) = 0.4881, σ = 0.0005,

t_+(corr.)= 0.4877.

KNO_3 (0.010420 M at -55.0°C.) I = 0.3856 mA.

Marks	Time	t_+	Marks	Time	t_+
16 - 8	2264	0.4841	14 - 3	3114	0.4848
16 - 7	2547	0.4849	14 - 2	3396	0.4855
16 - 6	2830	0.4852	14 - 1	3678	0.4849
16 - 5	3114	0.4851	14 - 5	2266	0.4853
16 - 4	3395	0.4857	13 - 4	2547	0.4860
16 - 3	3679	0.4851	13 - 3	2831	0.4852
16 - 2	3961	0.4854	13 - 2	3113	0.4857
16 - 1	4239	0.4856	13 - 1	3395	0.4852
15 - 7	2264	0.4850	12 - 4	2266	0.4859
15 - 6	2547	0.4853	12 - 3	2548	0.4854
15 - 5	2831	0.4852	12 - 2	2831	0.4855
15 - 4	3112	0.4858	12 - 1	3113	0.4852
15 - 3	3396	0.4851	11 - 3	2266	0.4854
15 - 2	3678	0.4853	11 - 2	2549	0.4855
15 - 1	3960	0.4852	11 - 1	2830	0.4854
14 - 6	2265	0.4849	10 - 2	2267	0.4858
14 - 5	2549	0.4848	10 - 1	2550	0.4849
14 - 4	2830	0.4855			

t_+(ave.) = 0.4853, σ = 0.0003,

t_+(corr.)= 0.4849.

KNO_3 (0.10736 M at -65.0°C.) I = 2.824 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 8	2617	0.4911	15 - 3	3483	0.4928
17 - 7	2907	0.4920	15 - 2	3772	0.4931
17 - 6	3195	0.4927	15 - 1	4062	0.4928
17 - 5	3483	0.4930	14 - 5	2608	0.4937
17 - 4	3773	0.4933	14 - 4	2898	0.4940
17 - 3	4064	0.4928	14 - 3	3189	0.4932
17 - 2	4353	0.4928	14 - 2	3478	0.4940
17 - 1	4643	0.4928	14 - 1	3768	0.4932
16 - 7	2617	0.4917	13 - 4	2608	0.4945
16 - 6	2905	0.4925	13 - 3	2900	0.4935
16 - 5	3193	0.4830	13 - 2	3189	0.4940
16 - 4	3483	0.4933	13 - 1	3478	0.4935
16 - 3	3774	0.4927	12 - 3	2607	0.4942
16 - 2	4063	0.4931	12 - 2	2896	0.4845
16 - 1	4353	0.4927	12 - 1	3186	0.4940
15 - 6	2615	0.4925	11 - 2	2607	0.4946
15 - 5	2902	0.4931	11 - 1	2898	0.4939
15 - 4	3192	0.4935	10 - 1	2607	0.4942

t_+(ave.) = 0.4932, σ = 0.0008,

t_+(corr.)= 0.4928.

KNO_3 (0.072851 M at -65.0°C.) I = 1.845 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 8	2718	0.4912	15 - 3	3628	0.4915
17 - 7	3024	0.4913	15 - 2	3929	0.4917
17 - 6	3325	0.4917	15 - 1	4230	0.4916
17 - 5	3626	0.4919	14 - 5	2724	0.4910
17 - 4	3927	0.4925	14 - 4	3025	0.4916
17 - 3	4229	0.4919	14 - 3	3320	0.4921
17 - 2	4530	0.4921	14 - 2	3628	0.4919
17 - 1	4832	0.4918	14 - 1	3926	0.4917
16 - 7	2720	0.4914	13 - 4	2724	0.4918
16 - 6	3024	0.4915	13 - 3	3024	0.4916
16 - 5	3325	0.4917	13 - 2	3322	0.4926
16 - 4	3626	0.4922	13 - 1	3627	0.4915
16 - 3	3928	0.4917	12 - 3	2720	0.4921
16 - 2	4229	0.4921	12 - 2	3025	0.4918
16 - 1	4531	0.4917	12 - 1	3323	0.4920
15 - 6	2722	0.4915	11 - 2	2721	0.4923
15 - 5	3025	0.4914	11 - 1	3024	0.4916
15 - 4	3326	0.4920	10 - 1	2720	0.4920

t_+(ave.) = 0.4919, σ = 0.0003,

t_+(corr.)= 0.4915

KNO_3 (0.036474 M at -65.0°C.) I = 0.9604 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2338	0.4884	15 - 4	3212	0.4900
17 - 8	2629	0.4884	15 - 3	3502	0.4897
17 - 7	2922	0.4890	15 - 2	3794	0.4898
17 - 6	3215	0.4892	14 - 6	2337	0.4892
17 - 5	3506	0.4894	14 - 5	2628	0.4895
17 - 4	3798	0.4897	14 - 4	2920	0.4899
17 - 3	4088	0.4895	14 - 3	3210	0.4896
17 - 2	4380	0.4896	14 - 2	3502	0.4901
16 - 8	2335	0.4886	13 - 5	2336	0.4900
16 - 7	2628	0.4892	13 - 4	2628	0.4903
16 - 8	2921	0.4894	13 - 3	2918	0.4900
16 - 5	3212	0.4896	13 - 2	3210	0.4903
16 - 4	3504	0.4898	12 - 4	2336	0.4906
16 - 3	3794	0.4896	12 - 3	2628	0.4899
16 - 2	4086	0.4899	12 - 2	2918	0.4904
15 - 7	2336	0.4892	11 - 3	2334	0.4906
15 - 6	2629	0.4894	11 - 2	2626	0.4906
15 - 5	2920	0.4897			

t_+(ave.) = 0.4897, σ = 0.0005,

t_+(corr.)= 0.4893.

KNO_3 (0.011286 M at -65.0°C.) I = 0.3463 mA.

Marks	Time	t_+	Marks	Time	t_+
16 - 8	2005	0.4883	14 - 3	2771	0.4867
16 - 7	2256	0.4890	14 - 2	3023	0.4872
16 - 6	2514	0.4879	14 - 1	3275	0.4864
16 - 5	2766	0.4879	13 - 5	2017	0.4870
16 - 4	3021	0.4876	13 - 4	2272	0.4867
16 - 3	3271	0.4874	13 - 3	2522	0.4865
16 - 2	3525	0.4875	13 - 2	2774	0.4869
16 - 1	3775	0.4871	13 - 1	3026	0.4863
15 - 7	2007	0.4887	12 - 4	2019	0.4872
15 - 6	2256	0.4894	12 - 3	2269	0.4869
15 - 5	2517	0.4874	12 - 2	2524	0.4865
15 - 4	2772	0.4872	12 - 1	2777	0.4859
15 - 3	3022	0.4870	11 - 3	2024	0.4854
15 - 2	3274	0.4870	11 - 2	2275	0.4860
15 - 1	3526	0.4867	11 - 1	2527	0.4856
14 - 6	2014	0.4871	10 - 2	2024	0.4858
14 - 5	2266	0.4871	10 - 1	2276	0.4853
14 - 4	2521	0.4869			

t_+(ave.) = 0.4870, σ = 0.0009,

t_+(corr.)= 0.4866.

NH_4NO_3 (0.15916M at -45.0°C) I = 5.250 mA

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2245	0.4060	15 - 2	3659	0.4054
17 - 8	2528	0.4055	15 - 1	3943	0.4049
17 - 7	2811	0.4058	14 - 6	2247	0.4062
17 - 6	3095	0.4056	14 - 5	2528	0.4062
17 - 5	3376	0.4057	14 - 4	2812	0.4061
17 - 4	3660	0.4056	14 - 3	3094	0.4055
17 - 3	3942	0.4052	14 - 2	3376	0.4059
17 - 2	4224	0.4053	14 - 1	3660	0.4049
17 - 1	4508	0.4048	13 - 5	2247	0.4067
16 - 8	2245	0.4057	13 - 4	2529	0.4068
16 - 7	2528	0.4060	13 - 3	2812	0.4059
16 - 6	2812	0.4058	13 - 2	3094	0.4061
16 - 5	3093	0.4059	13 - 1	3377	0.4054
16 - 4	3377	0.4058	12 - 4	2247	0.4072
16 - 3	3659	0.4053	12 - 3	2530	0.4062
16 - 2	3941	0.4054	12 - 2	2811	0.4063
16 - 1	4225	0.4048	12 - 1	3095	0.4056
15 - 7	2246	0.4062	11 - 3	2248	0.4066
15 - 6	2530	0.4060	11 - 2	2531	0.4064
15 - 5	2811	0.4060	11 - 1	2813	0.4058
15 - 4	3095	0.4059	10 - 2	2248	0.4069
15 - 3	3377	0.4054	10 - 1	2531	0.4060

t_+(ave.) = 0.4058, σ = 0.00052

t_+(corr.) = 0.4054

NH_4NO_3 (0.093307M at -45.0°C) I = 2.910 mA

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2666	0.4066	15 - 3	3550	0.4078
17 - 7	2961	0.4073	15 - 2	3850	0.4074
17 - 6	3256	0.4077	15 - 1	4148	0.4070
17 - 5	3553	0.4076	14 - 5	2662	0.4079
17 - 4	3851	0.4076	14.- 4	2960	0.4079
17 - 3	4148	0.4072	14 - 3	3257	0.4073
17 - 2	4445	0.4073	14 - 2	3554	0.4077
17 - 1	4753	0.4060	14 - 1	3854	0.4066
16 - 7	2663	0.4075	13 - 4	2664	0.4083
16 - 6	2958	0.4079	13 - 3	2961	0.4076
16 - 5	2255	0.4078	13 - 2	3258	0.4078
16 - 4	3553	0.4078	13 - 1	3556	0.4071
16 - 3	3850	0.4073	12 - 3	2667	0.4075
16 - 2	4147	0.4075	12 - 2	2964	0.4075
16 - 1	4445	0.4069	12 - 1	3262	0.4069
15 - 6	2661	0.4082	11 - 2	2668	0.4077
15 - 5	2958	0.4080	11 - 1	2965	0.4071
15 - 4	3256	0.4080	10 - 1	2668	0.4073

$t+(ave.) = 0.4075$, $\sigma = 0.00045$,

$t_+(corr.) = 0.4071$.

NH_4NO_3 (0.052124M at - 45.0°C) I = 1.6953 mA

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2263	0.4085	15 - 2	3677	0.4091
17 - 8	2546	0.4083	15 - 1	3961	0.4088
17 - 7	2829	0.4089	14 - 6	3265	0.4086
17 - 6	3113	0.4090	14 - 5	2546	0.4090
17 - 5	3394	0.4092	14 - 4	2830	0.4092
17 - 4	3678	0.4093	14 - 3	3112	0.4088
17 - 3	3960	0.4083	14 - 2	3394	0.4094
17 - 2	4242	0.4092	14 - 1	3678	0.4087
17 - 1	4526	0.4089	13 - 5	2265	0.4091
16 - 8	2263	0.4081	13 - 4	2547	0.4096
16 - 7	2546	0.4088	13 - 3	2830	0.4090
16 - 6	2830	0.4089	13 - 2	3112	0.4094
16 - 5	3111	0.4092	13 - 1	3395	0.4089
16 - 4	3395	0.4093	12 - 4	2265	0.4096
16 - 3	3677	0.4090	12 - 3	2548	0.4090
16 - 2	3959	0.4093	12 - 2	2829	0.4094
16 - 1	4243	0.4088	12 - 1	3113	0.4089
15 - 7	2264	0.4087	11 - 3	2266	0.4090
15 - 6	2548	0.4088	11 - 2	2549	0.4092
15 - 5	2829	0.4092	11 - 1	2831	0.4089
15 - 4	3113	0.4093	10 - 2	2266	0.4093
15 - 3	3395	0.4090	10 - 1	2549	0.4088

t_+(ave.) = 0.4090 σ = 0.0003

t_+(corr.) = 0.4086

NH_4NO_3 (0.031362M at -45.0°) I = 1.0441 mA

Marks	Time	t+	Marks	Time	t+
17 - 9	2202	0.4101	15 - 4	3027	0.4112
17 - 8	2476	0.4102	15 - 3	3304	0.4105
17 - 7	2750	0.4109	15 - 2	3579	0.4106
17 - 6	3023	0.4114	14 - 6	2208	0.4095
17 - 5	3296	0.4117	14 - 5	2480	0.4102
17 - 4	3573	0.4116	14 - 4	2756	0.4105
17 - 3	3848	0.4112	14 - 3	3032	0.4099
17 - 2	4123	0.4113	14 - 2	3307	0.4105
16 - 8	2204	0.4094	13 - 5	2207	0.4098
16 - 7	2478	0.4104	13 - 4	2484	0.4103
16 - 6	2751	0.4109	13 - 3	2759	0.4099
16 - 5	3024	0.4112	13 - 2	3034	0.4103
16 - 4	3301	0.4112	12 - 4	2212	0.4098
16 - 3	3576	0.4109	12 - 3	2487	0.4094
16 - 2	3851	0.4111	12 - 2	2762	0.4097
15 - 7	2206	0.4098	11 - 3	2213	0.4092
15 - 6	2479	0.4105	11 - 2	2488	0.4096
15 - 5	2752	0.4109	10 - 2	2215	0.4090

t_+(ave.) = 0.4105 σ = 0.00071

t_+(corr.) = 0.4101

NH_4NO_3 (0.014448M at - 45.0°C) I = 0.4831 mA

Marks	Time	t+	Marks	Time	t+
17 - 9	2180	0.4125	15 - 4	3006	0.4122
17 - 8	2454	0.4120	15 - 3	3281	0.4116
17 - 7	2728	0.4124	15 - 2	3557	0.4114
17 - 6	3001	0.4126	14 - 6	2185	0.4120
17 - 5	3274	0.4126	14 - 5	2459	0.4119
17 - 4	3551	0.4124	14 - 4	2735	0.4118
17 - 3	3826	0.4118	14 - 3	3010	0.4111
17 - 2	4101	0.4117	14 - 2	3285	0.4115
16 - 8	2182	0.4117	13 - 5	2185	0.4125
16 - 7	2456	0.4122	13 - 4	2462	0.4122
16 - 6	2729	0.4125	13 - 3	2727	0.4114
16 - 5	3002	0.4125	13 - 2	3012	0.4115
16 - 4	3279	0.4122	12 - 4	2190	0.4121
16 - 3	3554	0.4116	12 - 3	2465	0.4113
16 - 2	3829	0.4116	12 - 2	2740	0.4112
15 - 7	2184	0.4121	11 - 3	2191	0.4115
15 - 6	2457	0.4123	11 - 2	2466	0.4114
15 - 5	2730	0.4124	10 - 2	2193	0.4114

t+(ave.) = 0.4119 σ = 0.00043

t+(corr.) = 0.4115

NH_4NO_3 (0.007896M at - 45.0°C) I = 0.2418 mA

Marks	Time	t_+	Marks	Time	t_+
17 - 9	3375	0.4137	15 - 4	3381	0.4134
17 - 8	3673	0.3130	15 - 3	3581	0.4118
17 - 7	3973	0.4132	15 - 2	3882	0.4115
17 - 6	3374	0.4130	14 - 6	2382	0.4126
17 - 5	3575	0.3127	14 - 5	2683	0.4122
17 - 4	3875	0.4126	14 - 4	2984	0.4121
17 - 3	4175	0.4121	14 - 3	3285	0.4115
17 - 2	4477	0.4118	14 - 2	3587	0.4114
16 - 8	3376	0.4128	13 - 5	3387	0.4123
16 - 7	3676	0.4131	13 - 4	3688	0.4122
16 - 6	3976	0.4130	13 - 3	3988	0.4114
16 - 5	3277	0.4126	13 - 2	3390	0.4113
16 - 4	3578	0.4125	12 - 4	3394	0.4117
16 - 3	3879	0.4117	12 - 3	3693	0.4110
16 - 2	4180	0.4117	12 - 2	3993	0.4110
15 - 7	3379	0.4131	11 - 3	3395	0.4111
15 - 6	3680	0.4128	11 - 2	3696	0.4109
15 - 5	3980	0.4125			

t_+(ave.) = 0.4121 σ = 0.00071

t_+ (corr.) = 0.4117

NH_4NO_3 (0.15156M at - 55.0°C). I = 5.369 mA

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2159	0.3931	15 - 2	3525	0.3918
17 - 8	2432	0.3924	15 - 1	3798	0.3914
17 - 7	2704	0.3927	14 - 6	2164	0.3927
17 - 6	2975	0.3929	14 - 5	2437	0.3923
17 - 5	3248	0.3926	14 - 4	2711	0.3922
17 - 4	3522	0.3924	14 - 3	2984	0.3915
17 - 3	3795	0.3919	14 - 2	3256	0.3918
17 - 2	4067	0.3919	14 - 1	3529	0.3910
17 - 1	4340	0.3915	13 - 5	2166	0.3928
16 - 8	2161	0.3924	13 - 4	2440	0.3925
16 - 7	2433	0.3928	13 - 3	2713	0.3917
16 - 6	2704	0.3929	13 - 2	2985	0.3919
16 - 5	2977	0.3926	13 - 1	3258	0.3912
16 - 4	3251	0.3924	12 - 4	2167	0.3931
16 - 3	3524	0.3918	12 - 3	2440	0.3921
16 - 2	3796	0.3919	12 - 2	2712	0.3921
16 - 1	4069	0.3914	12 - 1	2985	0.3921
15 - 7	2162	0.3929	11 - 3	2170	0.3922
15 - 6	2453	0.3930	11 - 2	2442	0.3921
15 - 5	2706	0.3927	11 - 1	2715	0.3915
15 - 4	2980	0.3925	10 - 2	2171	0.3922
15 - 3	3253	0.3919	10 - 1	2444	0.3915

t_+(ave.) = 0.3921 σ = 0.00054

t_+(corr.) = 0.3918

NH_4NO_3 (0.091930 M at -55.0°C.) I = 2.695 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 8	2919	0.3951	15 - 3	3893	0.3957
17 - 7	3242	0.3958	15 - 2	4218	0.3957
17 - 6	3568	0.3959	15 - 1	4544	0.3953
17 - 5	3892	0.3959	14 - 5	2917	0.3960
17 - 4	4217	0.3960	14 - 4	3242	0.3956
17 - 3	4543	0.3956	14 - 3	3568	0.3956
17 - 2	4868	0.3956	14 - 2	3893	0.3960
17 - 1	5193	0.3954	14 - 1	4219	0.3952
16 - 7	2917	0.3959	13 - 4	2918	0.3966
16 - 6	3243	0.3959	13 - 3	3244	0.3959
16 - 5	3567	0.3960	13 - 2	3569	0.3961
16 - 4	3892	0.3961	13 - 1	3895	0.3954
16 - 3	4218	0.3956	12 - 3	2920	0.3959
16 - 2	4543	0.3957	12 - 2	3245	0.3960
16 - 1	4869	0.3953	12 - 1	3571	0.3955
15 - 6	2918	0.3960	11 - 2	2920	0.3963
15 - 5	3242	0.3961	11 - 1	3246	0.3957
15 - 4	3567	0.3962	10 - 1	2922	0.3957

t_+(ave.) = 0.3957, σ = 0.0003

t_+(corr.)= 0.3954.

NH_4NO_3 (0.044982 M at -55.0°C.) I = 1.2568 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2691	0.3999	15 - 2	4380	0.3998
17 - 8	3029	0.3995	15 - 1	4717	0.3996
17 - 7	3364	0.4003	14 - 6	2694	0.3999
17 - 6	3699	0.4006	14 - 5	3026	0.4006
17 - 5	4035	0.4007	14 - 4	3366	0.4005
17 - 4	4373	0.4007	14 - 3	3706	0.3996
17 - 3	4711	0.4002	14 - 2	4045	0.3999
17 - 2	5050	0.4001	14 - 1	4379	0.3995
17 - 1	5389	0.3997	13 - 5	2696	0.4001
16 - 8	2694	0.3991	13 - 4	3034	0.4003
16 - 7	3029	0.4000	13 - 3	3374	0.3994
16 - 6	3364	0.4004	13 - 2	3713	0.3995
16 - 5	3698	0.4007	13 - 1	4046	0.3994
16 - 4	4036	0.4008	12 - 4	2696	0.4006
16 - 3	4376	0.4000	12 - 3	3036	0.3996
16 - 2	4715	0.4000	12 - 2	3375	0.3995
16 - 1	5054	0.3995	12 - 1	3712	0.3992
15 - 7	2694	0.3998	11 - 3	2701	0.3995
15 - 6	3029	0.4003	11 - 2	3038	0.3997
15 - 5	3365	0.4004	11 - 1	3373	0.3995
15 - 4	3703	0.4005	10 - 2	2702	0.3996
15 - 3	4041	0.3999	10 - 1	3038	0.3993

t_+(ave.) = 0.4000, σ = 0.00045

t_+(corr.)= 0.3997.

NH_4NO_3 (0.014522 M at -55.0°C.) I = 0.5923 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 8	2052	0.4040	15 - 3	2742	0.4038
17 - 7	2280	0.4045	15 - 2	2971	0.4038
17 - 6	2510	0.4045	15 - 1	3201	0.4034
17 - 5	2738	0.4045	14 - 6	2058	0.4035
17 - 4	2968	0.4045	14 - 4	2288	0.4036
17 - 3	3195	0.4043	14 - 3	2515	0.4034
17 - 2	3424	0.4043	14 - 2	2744	0.4039
17 - 1	3654	0.4038	14 - 1	2970	0.4036
16 - 7	2054	0.4041	13 - 4	2060	0.4039
16 - 6	2284	0.4040	13 - 3	2287	0.4036
16 - 5	2512	0.4041	13 - 2	2516	0.4039
16 - 4	2742	0.4041	13 - 1	2744	0.4035
16 - 3	2969	0.4039	12 - 3	2058	0.4039
16 - 2	3198	0.4040	12 - 2	2286	0.4041
16 - 1	3428	0.4035	12 - 1	2514	0.4038
15 - 6	2057	0.4038	11 - 2	2058	0.4041
15 - 5	2285	0.4040	11 - 1	2286	0.4038
15 - 4	2513	0.4043	10 - 1	2058	0.4038

t_+(ave.) = 0.4040, σ = 0.00032,

t_+(corr.)= 0.4037.

NH_4NO_3 (0.008932 M at -55.0°C.) I = 0.2813 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2361	0.4044	15 - 2	3829	0.4057
17 - 8	2654	0.4045	14 - 6	2359	0.4052
17 - 7	2950	0.4050	14 - 5	2654	0.4053
17 - 6	3244	0.4053	14 - 4	2947	0.4058
17 - 5	3539	0.4053	14 - 3	3240	0.4055
17 - 4	3832	0.4057	14 - 2	3534	0.4061
17 - 3	4125	0.4055	13 - 5	2360	0.4055
17 - 2	4419	0.4057	13 - 4	2654	0.4059
16 - 8	2360	0.4042	13 - 3	2945	0.4059
16 - 7	2656	0.4047	13 - 2	3241	0.4060
16 - 6	2950	0.4051	12 - 4	2362	0.4057
16 - 5	3245	0.4052	12 - 3	2651	0.4060
16 - 4	3538	0.4056	12 - 2	2947	0.4059
16 - 3	3831	0.4054	11 - 3	2360	0.4056
16 - 2	4125	0.4057	11 - 2	2654	0.4059
15 - 7	2360	0.4049	10 - 2	2362	0.4055
15 - 6	2654	0.4053	15 - 5	2949	0.4054
15 - 3	3535	0.4056	15 - 4	3242	0.4059

t_+(ave.) = 0.4055, σ = 0.00044,

t_+(corr.)= 0.4051.

NH_4NO_3 (0.15645 M at -65.0°C.) I = 5.263 mA.

Marks	Time	t_+	Marks	Time	t_+
16 - 8	2344	0.3810	14 - 3	3222	0.3818
16 - 7	2638	0.3815	14 - 2	3516	0.3821
16 - 6	2929	0.3820	14 - 1	3811	0.3813
16 - 5	3223	0.3819	13 - 5	2347	0.3817
16 - 4	3516	0.3821	13 - 4	2640	0.3821
16 - 3	3805	0.3821	13 - 3	2929	0.3821
16 - 2	4099	0.3822	13 - 2	3223	0.3815
16 - 1	4394	0.3817	13 - 1	3518	0.3815
15 - 7	2346	0.3813	12 - 4	2348	0.3820
15 - 6	2639	0.3816	12 - 3	2639	0.3818
15 - 5	2933	0.3816	12 - 2	2932	0.3819
15 - 4	3226	0.3818	12 - 1	3228	0.3813
15 - 3	3515	0.3819	11 - 3	2346	0.3820
15 - 2	3809	0.3818	11 - 2	2640	0.3819
15 - 1	4104	0.3814	11 - 1	2933	0.3815
14 - 6	2346	0.3814	10 - 2	2348	0.3819
14 - 5	2640	0.3814	10 - 1	2641	0.3815
14 - 4	2933	0.3817			

t_+(ave.) = 0.3818, σ = 0.0003,

t_+(corr.)= 0.3815.

NH_4NO_3 (0.094302 M at -65.0°C.) I = 2.786 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2632	0.3867	15 - 4	3630	0.3864
17 - 8	2963	0.3862	15 - 3	3959	0.3861
17 - 7	3293	0.3867	15 - 2	4287	0.3863
17 - 6	3617	0.3875	14 - 6	2634	0.3869
17 - 5	3950	0.3871	14 - 5	2967	0.3865
17 - 4	4285	0.3868	14 - 4	3299	0.3865
17 - 3	4614	0.3865	14 - 3	3627	0.3862
17 - 2	4942	0.3867	14 - 2	3958	0.3865
16 - 8	2632	0.3863	13 - 5	2634	0.3873
16 - 7	2962	0.3868	13 - 4	2968	0.3870
16 - 6	3286	0.3877	13 - 3	3300	0.3862
16 - 5	3619	0.3872	13 - 2	3628	0.3867
16 - 4	3954	0.3869	12 - 4	2638	0.3872
16 - 2	4611	0.3868	12 - 3	2969	0.3865
16 - 3	4283	0.3865	12 - 2	3300	0.3865
15 - 7	2638	0.3861	11 - 3	2638	0.3868
15 - 6	2962	0.3871	11 - 2	2969	0.3868
15 - 5	3295	0.3867	10 - 2	2639	0.3869

t_+(ave.) = 0.3867, σ = 0.0004,

t_+(corr.) = 0.3864.

NH_4NO_3 (0.046593 M at -65.0°C.) I = 1.7128 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2189	0.3915	15 - 2	3398	0.3917
17 - 8	2351	0.3912	15 - 1	3662	0.3912
17 - 7	2612	0.3918	14 - 6	2093	0.3913
17 - 6	2875	0.3918	14 - 5	2353	0.3916
17 - 5	3135	0.3920	14 - 4	2615	0.3918
17 - 4	3397	0.3921	14 - 3	2875	0.3915
17 - 3	3657	0.3919	14 - 2	3137	0.3919
17 - 2	3919	0.3919	14 - 1	3400	0.3911
17 - 1	4182	0.3915	13 - 5	2093	0.3917
16 - 8	2091	0.3908	13 - 4	2355	0.3919
16 - 7	2352	0.3915	13 - 3	2615	0.3917
16 - 6	2615	0.3915	13 - 2	2877	0.3919
16 - 5	2875	0.3918	13 - 1	3140	0.3912
16 - 4	3137	0.3919	12 - 4	2094	0.3920
16 - 3	3397	0.3917	12 - 3	2354	0.3917
16 - 2	3659	0.3918	12 - 2	2616	0.3918
16 - 1	3922	0.3913	12 - 1	2878	0.3917
15 - 7	2091	0.3915	11 - 3	2094	0.3917
15 - 6	2354	0.3915	11 - 2	2354	0.3920
15 - 5	2614	0.3918	11 - 1	2617	0.3914
15 - 4	2876	0.3920	10 - 2	2093	0.3920
15 - 3	3136	0.3917	10 - 1	2355	0.3915

t_+(ave.) = 0.3917, σ = 0.0003,

t_+(corr.)= 0.3914.

NH_4NO_3 (0.017962 M at -65.0°C.) I = 0.5949 mA

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2292	0.3961	15 - 2	3723	0.3968
17 - 8	2579	0.3958	15 - 1	4009	0.3966
17 - 7	2863	0.3968	14 - 6	2292	0.3966
17 - 6	3148	0.3971	14 - 5	2578	0.3967
17 - 5	3455	0.3970	14 - 4	2866	0.3968
17 - 4	3723	0.3971	14 - 3	3153	0.3963
17 - 3	4010	0.3967	14 - 2	3439	0.3968
17 - 2	4296	0.3968	14 - 1	3724	0.3963
17 - 1	4580	0.3968	13 - 5	2293	0.3969
16 - 8	2293	0.3956	13 - 4	2581	0.3969
16 - 7	2577	0.3966	13 - 3	2868	0.3964
16 - 6	2862	0.3971	13 - 2	3154	0.3967
16 - 1	4295	0.3966	13 - 1	3439	0.3964
16 - 5	3150	0.3969	12 - 4	2297	0.3967
16 - 4	3436	0.3971	12 - 3	2584	0.3961
16 - 3	3724	0.3966	12 - 2	2869	0.3965
16 - 2	4010	0.3968	12 - 1	3155	0.3960
15 - 7	4295	0.3966	11 - 3	2299	0.3960
15 - 6	2578	0.3968	11 - 2	2584	0.3964
15 - 5	2863	0.3970	11 - 1	2870	0.3961
15 - 4	3151	0.3971	10 - 2	2299	0.3962
15 - 3	3438	0.3966	10 - 1	2584	0.3961

t_+(ave.) = 0.3967, σ = 0.0003,

t_+(corr.)= 0.3964.

NH_4NO_3 (0.015810 M at -65.0°C.) I = 0.5110 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 8	2635	0.3970	15 - 3	3519	0.3970
17 - 7	2928	0.3975	15 - 2	3813	0.3970
17 - 6	3221	0.3977	15 - 1	4107	0.3967
17 - 5	3515	0.3976	14 - 5	2638	0.3972
17 - 4	3809	0.3977	14 - 4	2932	0.3974
17 - 3	4101	0.3972	14 - 3	3227	0.3967
17 - 2	4398	0.3972	14 - 2	3521	0.3971
17 - 1	4692	0.3969	14 - 1	3815	0.3964
16 - 7	2636	0.3973	13 - 4	2640	0.3976
16 - 6	2929	0.3976	13 - 3	2935	0.3969
16 - 5	3223	0.3974	13 - 2	3229	0.3971
16 - 4	3517	0.3976	13 - 1	3523	0.3966
16 - 3	3812	0.3970	12 - 3	2643	0.3968
16 - 2	4106	0.3971	12 - 2	2937	0.3969
16 - 1	4400	0.3967	12 - 1	3231	0.3965
15 - 6	2636	0.3976	11 - 2	2646	0.3967
15 - 5	2930	0.3975	11 - 1	2940	0.3962
15 - 4	3224	0.3976	10 - 1	2647	0.3962

t_+(ave.) = 0.3972, σ = 0.0004,

t_+(corr.)= 0.3969.

NH_4NO_3 (0.006420 M at -65.0°C.) I = 0.2126 mA.

Marks	Time	t_+	Marks	Time	t_+
16 - 8	2265	0.4004	14 - 3	3132	0.3990
16 - 7	2547	0.4013	14 - 2	3416	0.3995
16 - 6	2833	0.4011	14 - 1	3700	0.3990
16 - 5	3121	0.4006	13 - 5	2275	0.4000
16 - 4	3409	0.4003	13 - 4	2563	0.3997
16 - 3	3694	0.3998	13 - 3	2848	0.3992
16 - 2	3978	0.4000	13 - 2	3132	0.3996
16 - 1	4264	0.3995	13 - 1	3418	0.3990
15 - 7	2270	0.4005	12 - 4	2280	0.3997
15 - 6	2556	0.4002	12 - 3	2565	0.3991
15 - 5	2841	0.4001	12 - 2	2849	0.3993
15 - 4	3128	0.4000	12 - 1	3134	0.3990
15 - 3	3414	0.3994	11 - 3	2281	0.3991
15 - 2	3696	0.3997	11 - 2	2565	0.3994
15 - 1	3982	0.3993	11 - 1	2849	0.3991
14 - 6	2273	0.3999	10 - 2	2280	0.3995
14 - 5	2561	0.3993	10 - 1	2565	0.3990
14 - 4	2848	0.3993			

t_+(ave.) = 0.3997, σ = 0.0005,

t_+(corr.)= 0.3994.

$NaNO_3$ (0.096427 M at -45.0°C.) I = 2.688 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	3683	0.4020	15 - 2	4374	0.4013
17 - 8	3023	0.4012	15 - 1	4713	0.4008
17 - 7	3358	0.4019	14 - 6	2688	0.4018
17 - 6	3693	0.4022	14 - 5	3022	0.4006
17 - 5	4027	0.4024	14 - 4	3360	0.4021
17 - 4	4365	0.4024	14 - 3	3700	0.4012
17 - 3	4705	0.4017	14 - 2	4039	0.4014
17 - 2	5044	0.4016	14 - 1	4375	0.4008
17 - 1	5383	0.4011	13 - 5	2690	0.4019
16 - 8	2688	0.4009	13 - 4	3028	0.4020
16 - 7	3023	0.4017	13 - 3	3368	0.4010
16 - 6	3358	0.4021	13 - 2	3707	0.4011
16 - 5	3692	0.4023	13 - 1	4042	0.4007
16 - 4	4030	0.4023	12 - 4	2690	0.4024
16 - 3	4370	0.4015	12 - 3	3030	0.4013
16 - 2	4709	0.4014	12 - 2	3369	0.4012
16 - 1	5048	0.4009	12 - 1	3708	0.4006
15 - 7	2688	0.4016	11 - 3	2695	0.4013
15 - 6	3023	0.4020	11 - 2	3031	0.4015
15 - 5	3357	0.4023	11 - 1	3370	0.4008
15 - 4	3695	0.4023	10 - 2	2696	0.4014
15 - 3	4035	0.4014	10 - 1	3032	0.4010

t_+(ave.) = 0.4016, σ = 0.0005,

t_+(corr.)= 0.4013.

$NaNO_3$ (0.053147 M at -45.0°C.) I = 1.7426 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2260	0.4057	15 - 2	3674	0.4057
17 - 8	2543	0.4055	15 - 1	3958	0.4058
17 - 7	2826	0.4060	14 - 6	2262	0.4058
17 - 6	3110	0.4061	14 - 5	2543	0.4062
17 - 5	3391	0.4063	14 - 4	2827	0.4063
17 - 4	3675	0.4063	14 - 3	3109	0.4059
17 - 3	3957	0.4060	14 - 2	3391	0.4064
17 - 2	4239	0.4062	14 - 1	3675	0.4057
17 - 1	4523	0.4058	13 - 5	2262	0.4067
16 - 8	2260	0.4053	13 - 4	2544	0.4067
16 - 7	2543	0.4060	13 - 3	2827	0.4061
16 - 6	2827	0.4060	13 - 2	3109	0.4065
16 - 5	3108	0.4063	13 - 1	3392	0.4059
16 - 4	3392	0.4062	12 - 4	2262	0.4069
16 - 3	3674	0.4060	12 - 3	2545	0.4062
16 - 2	3956	0.4063	12 - 2	2826	0.4065
16 - 1	4240	0.4058	12 - 1	3110	0.4060
15 - 7	2261	0.4059	11 - 3	2263	0.4063
15 - 6	2545	0.4060	11 - 2	2546	0.4063
15 - 5	2826	0.4062	11 - 1	2828	0.4060
15 - 4	3110	0.4063	10 - 2	2263	0.4065
15 - 3	3392	0.4063	10 - 1	2546	0.4060

t_+(ave.) = 0.4061, σ = 0.0003,

t_+(corr.)= 0.4057.

$NaNO_3$ (0.035571 M at -45.0°C.) I = 1.2091 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2166	0.4083	15 - 2	3532	0.4075
17 - 8	2439	0.4078	15 - 1	3805	0.4072
17 - 7	2711	0.4082	14 - 6	2171	0.4079
17 - 6	2982	0.4085	14 - 5	2444	0.4077
17 - 5	3255	0.4083	14 - 4	2718	0.4076
17 - 4	3529	0.4082	14 - 3	2991	0.4070
17 - 3	3802	0.4076	14 - 2	3263	0.4075
17 - 2	4074	0.4077	14 - 1	3536	0.4067
17 - 1	4347	0.4073	13 - 5	2173	0.4080
16 - 8	2168	0.4076	13 - 4	2447	0.4079
16 - 7	2440	0.4082	13 - 3	2720	0.4072
16 - 6	2711	0.4084	13 - 2	2992	0.4075
16 - 5	2984	0.4082	13 - 1	3265	0.4069
16 - 4	3258	0.4081	12 - 4	2174	0.4084
16 - 3	3531	0.4075	12 - 3	2447	0.4075
16 - 2	3803	0.4077	12 - 2	2719	0.4076
16 - 1	4076	0.4072	12 - 1	2992	0.4071
15 - 7	2169	0.4082	11 - 3	2177	0.4074
15 - 6	2440	0.4084	11 - 2	2449	0.4070
15 - 5	2713	0.4082	11 - 1	2722	0.4070
15 - 4	2987	0.4081	10 - 2	2178	0.4075
15 - 3	3260	0.4075	10 - 1	2451	0.4069

t_+(ave.) = 0.4077, σ = 0.0004,

t_+(corr.)= 0.4074.

$NaNO_3$ (0.023008 M at -45.0°C.) I = 0.7733 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2182	0.4100	15 - 4	3007	0.4100
17 - 8	2456	0.4096	15 - 3	3284	0.4091
17 - 7	2730	0.4100	15 - 2	3559	0.4090
17 - 6	3003	0.4103	15 - 1	2187	0.4096
17 - 5	3276	0.4103	14 - 5	2460	0.4097
17 - 4	3553	0.4101	14 - 4	2737	0.4094
17 - 3	3828	0.4095	14 - 3	3012	0.4088
17 - 2	4103	0.4094	14 - 2	3287	0.4091
16 - 8	2184	0.4092	13 - 5	2187	0.4100
16 - 6	2731	0.4100	13 - 4	2464	0.4097
16 - 5	3004	0.4101	13 - 3	2739	0.4090
16 - 7	2458	0.4098	13 - 2	3014	0.4091
16 - 4	3281	0.4099	12 - 4	2192	0.4096
16 - 3	3556	0.4093	12 - 3	2467	0.4039
16 - 2	3831	0.4093	12 - 2	2742	0.4088
15 - 7	2186	0.4096	11 - 3	2193	0.4090
15 - 6	2459	0.4099	11 - 2	2468	0.4090
15 - 5	2732	0.4100	10 - 2	2195	0.4090

t_+(ave.) = 0.4095, σ = 0.0004,

t_+(corr.)= 0.4092.

$NaNO_3$ (0.012136 M at -45.0°C.) I = 0.4068 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2166	0.4141	15 - 4	2998	0.4123
17 - 8	2441	0.4132	15 - 3	3273	0.4116
17 - 7	2716	0.4132	15 - 2	3547	0.4115
17 - 6	2991	0.4130	14 - 6	2180	0.4120
17 - 5	3264	0.4129	14 - 5	2453	0.4119
17 - 4	3539	0.4127	14 - 4	2728	0.4119
17 - 3	3814	0.4121	14 - 3	3003	0.4111
17 - 2	4088	0.4120	14 - 2	3277	0.4114
16 - 8	2171	0.4127	13 - 3	2735	0.4107
16 - 7	2446	0.4128	13 - 5	2185	0.4115
16 - 6	2721	0.4126	13 - 4	2460	0.4115
16 - 5	2994	0.4125	13 - 3	3009	0.4109
16 - 4	3269	0.4124	12 - 4	2190	0.4111
16 - 3	3544	0.4117	12 - 3	2465	0.4103
16 - 2	3818	0.4118	12 - 2	2739	0.4104
15 - 7	2175	0.4127	11 - 3	2194	0.4100
15 - 6	2450	0.4125	11 - 2	2468	0.4101
15 - 5	2723	0.4124	10 - 2	2196	0.4099

t_+(ave.) = 0.4119. σ = 0.0010,

t_+(corr.)= 0.4116.

$NaNO_3$ (0.10860 M at -65.0°C.) I = 3.509 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2372	0.3923	15 - 4	3281	0.3904
17 - 8	2672	0.3916	15 - 5	2979	0.3913
17 - 7	2971	0.3919	15 - 3	3582	0.3905
17 - 6	3272	0.3917	14 - 6	2382	0.3911
17 - 5	3573	0.3913	14 - 5	2683	0.3907
17 - 4	3875	0.3911	14 - 4	2985	0.3905
17 - 3	4176	0.3905	14 - 3	3286	0.3898
17 - 2	4477	0.3904	14 - 2	3587	0.3900
16 - 8	2375	0.3914	13 - 5	2387	0.3908
16 - 7	2674	0.3918	13 - 4	2689	0.3905
16 - 6	2975	0.3915	13 - 3	2990	0.3897
16 - 5	3276	0.3912	13 - 2	3291	0.3898
16 - 4	3578	0.3910	12 - 4	2394	0.3902
16 - 3	3879	0.3903	12 - 3	2695	0.3893
16 - 2	4180	0.3902	12 - 2	2996	0.3892
15 - 7	2377	0.3918	11 - 3	2398	0.3891
15 - 6	2678	0.3916	11 - 2	2699	0.3891
15 - 2	3883	0.3900	10 - 2	2403	0.3887

$t_+(ave.) = 0.3905$, $\sigma = 0.0008$,

$t_+(corr.) = 0.3902$.

$NaNO_3$ (0.054132 M at -65.0°C.) I = 1.7610 mA.

Marks	Time	t_+	Marks	Time	t_+
16 - 8	2346	0.3936	14 - 3	3224	0.3945
16 - 7	2638	0.3945	14 - 2	3518	0.3949
16 - 6	2931	0.3947	14 - 1	3813	0.3941
16 - 5	3225	0.3947	13 - 5	2349	0.3944
16 - 4	3518	0.3949	13 - 4	2642	0.3941
16 - 3	3807	0.3950	13 - 3	2931	0.3950
16 - 2	4101	0.3950	13 - 2	3225	0.3950
16 - 1	4396	0.3945	13 - 1	3520	0.3943
15 - 7	2348	0.3940	12 - 4	2350	0.3935
15 - 6	2641	0.3943	12 - 3	2639	0.3948
15 - 5	2935	0.3943	12 - 2	2933	0.3949
15 - 4	3228	0.3946	12 - 1	3228	0.3943
15 - 3	3517	0.3947	11 - 3	2346	0.3950
15 - 2	3811	0.3946	11 - 2	2640	0.3950
15 - 1	4106	0.3942	11 - 1	2935	0.3943
14 - 6	2348	0.3941	10 - 2	2344	0.3956
14 - 5	2642	0.3941	10 - 1	2639	0.3948
14 - 4	2935	0.3945			

t_+(ave.) = 0.3945, σ = 0.0004,

t_+(corr.)= 0.3942.

$NaNO_3$ (0.025671 M at -65.0°C.) I = 0.8296 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2339	0.3978	15 - 2	3810	0.3974
17 - 8	2632	0.3975	15 - 1	4101	0.3971
17 - 7	2925	0.3980	14 - 6	2341	0.3980
17 - 6	3218	0.3982	14 - 5	2635	0.3978
17 - 5	3512	0.3981	14 - 4	2929	0.3979
17 - 4	3806	0.3981	14 - 3	3224	0.3972
17 - 3	4101	0.3976	14 - 2	3518	0.3976
17 - 2	4395	0.3976	14 - 1	3812	0.3968
17 - 1	4689	0.3972	13 - 5	2343	0.3981
16 - 8	2540	0.3972	13 - 4	2637	0.3982
16 - 7	2833	0.3979	13 - 3	2932	0.3974
16 - 6	2926	0.3982	13 - 2	3226	0.3976
16 - 5	3220	0.3979	13 - 1	3520	0.3969
16 - 4	3514	0.3980	12 - 4	2345	0.3983
16 - 3	3809	0.3974	12 - 3	2640	0.3973
16 - 2	4103	0.3975	12 - 2	2934	0.3974
16 - 1	4397	0.3971	12 - 1	3228	0.3969
15 - 7	2540	0.3980	11 - 3	2349	0.3971
15 - 6	2833	0.3982	11 - 2	2643	0.3972
15 - 5	2927	0.3980	11 - 1	2937	0.3967
15 - 4	3221	0.3981	10 - 2	2350	0.3973
15 - 3	3516	0.3974	10 - 1	2644	0.3967

t_+(ave.) = 0.3976, q = 0.0004,

t_+(corr.) = 0.3973.

$NaNO_3$ (0.014503 M at -65.0°C.) I = 0.4736 mA.

Marks	Time	t_+	Marks	Time	t_+
16 - 8	2263	0.4009	14 - 3	3134	0.3988
16 - 7	2547	0.4014	14 - 2	3417	0.3994
16 - 6	2833	0.4012	14 - 1	3704	0.3988
16 - 5	3121	0.4007	13 - 5	2276	0.3999
16 - 4	3408	0.4005	13 - 4	2563	0.3998
16 - 3	3694	0.3999	13 - 2	3132	0.3996
16 - 2	3977	0.4002	13 - 3	2849	0.3991
16 - 1	4264	0.3996	13 - 1	3419	0.3989
15 - 7	2267	0.4009	12 - 4	2280	0.3998
15 - 6	2553	0.4008	12 - 3	2566	0.3990
15 - 5	2841	0.4002	12 - 2	2849	0.3994
15 - 4	3128	0.4001	12 - 1	3136	0.3987
15 - 3	3414	0.3995	11 - 3	2282	0.3990
15 - 2	3697	0.3997	11 - 2	2565	0.3995
15 - 1	3984	0.3992	11 - 1	2852	0.3988
14 - 6	2275	0.4000	10 - 2	2280	0.3996
14 - 5	2561	0.3994	10 - 1	2567	0.3988
14 - 4	2848	0.3994			

t_+(ave.) = 0.3998, σ = 0.0007

t_+(corr.) = 0.3995.

$LiNO_3$ (0.10199 M at -45.0°C.) I = 3.742 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2327	0.3521	15 - 2	3780	0.3527
17 - 8	2617	0.3521	15 - 1	4072	0.3525
17 - 7	2906	0.3528	14 - 6	2324	0.3530
17 - 6	3198	0.3529	14 - 5	2616	0.3528
17 - 5	3490	0.3528	14 - 4	2906	0.3532
17 - 4	3780	0.3531	14 - 3	3198	0.3526
17 - 3	4072	0.3526	14 - 2	3490	0.3529
17 - 2	4364	0.3526	14 - 1	3782	0.3525
17 - 1	4656	0.3523	13 - 5	3325	0.3533
16 - 8	2325	0.3521	13 - 4	2616	0.3535
16 - 7	2614	0.3530	13 - 3	2907	0.3529
16 - 6	2906	0.3530	13 - 2	3199	0.3530
16 - 5	3198	0.3529	13 - 1	3491	0.3525
16 - 4	3488	0.3531	12 - 4	2326	0.3535
16 - 3	3780	0.3527	12 - 3	2616	0.3531
16 - 2	4072	0.3527	12 - 2	2908	0.3531
16 - 1	4364	0.3524	12 - 1	3200	0.3526
15 - 7	2322	0.3532	11 - 3	2326	0.3532
15 - 6	2614	0.3532	11 - 2	2618	0.3528
15 - 5	2906	0.3530	11 - 1	2910	0.3528
15 - 4	3198	0.3531	10 - 3	2327	0.3531
15 - 3	3488	0.3528	10 - 1	2618	0.3528

t_+(ave.) = 0.3528, σ = 0.0003,

t_+(corr.)= 0.3525.

$LiNO_3$ (0.055299 N at -45.0°C.) I = 1.3100 mA

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2208	0.3669	15 - 4	3036	0.3677
17 - 8	2483	0.3669	15 - 3	3313	0.3672
17 - 7	2759	0.3674	15 - 2	3590	0.3672
17 - 6	3036	0.3675	15 - 6	2208	0.3674
17 - 5	3313	0.3674	14 - 5	2485	0.3672
17 - 4	3590	0.3675	14 - 4	2762	0.3674
17 - 3	3867	0.3671	14 - 3	3038	0.3670
17 - 2	4144	0.3671	14 - 2	3316	0.3672
16 - 8	2207	0.3667	13 - 5	2209	0.3676
16 - 7	2483	0.3673	13 - 4	2486	0.3678
16 - 6	2760	0.7536	13 - 3	2763	0.3671
16 - 5	3037	0.3674	13 - 2	3040	0.3673
16 - 3	3591	0.3670	12 - 4	2210	0.3679
16 - 4	3314	0.3675	12 - 3	2487	0.3672
16 - 2	3868	0.3671	12 - 2	2764	0.3673
15 - 7	2207	0.3674	11 - 3	2210	0.3676
15 - 6	2482	0.3678	11 - 2	2487	0.3676
15 - 5	2759	0.3676	10 - 2	2212	0.3674

t_+(ave.) = 0.3673, σ = 0.0005

t_+(corr.) = 0.3670.

$LiNO_3$ (0.028519 M at -45.0°C.) I = 1.1021 mA.

Marks	Time	t_+	Marks	Time	t_+
16 -8	2103	0.3696	14 - 3	2903	0.3689
16 - 7	2366	0.3702	14 - 2	3166	0.3694
16 - 6	2631	0.3698	14 - 1	3430	0.3688
16 - 5	2897	0.3698	13 - 5	2111	0.3695
16 - 4	3163	0.3697	13 - 4	2377	0.3694
16 - 3	3428	0.3695	13 - 3	2642	0.3688
16 - 2	3691	0.3695	13 - 2	2905	0.3692
16 - 1	3955	0.3692	13 - 1	3169	0.3687
15 - 7	2101	0.3704	12 - 4	2115	0.3693
15 - 6	2366	0.3704	12 - 3	2380	0.3685
15 - 5	2632	0.3701	12 - 2	2643	0.3689
15 - 4	2898	0.3700	12 - 1	2907	0.3685
15 - 3	3163	0.3694	11 - 3	2113	0.3692
15 - 2	3426	0.3693	11 - 2	2376	0.3695
15 - 1	3690	0.3693	11 - 1	2640	0.3691
14 - 6	2106	0.3699	10 - 2	2113	0.3695
14 - 5	2372	0.3695	10 - 1	2377	0.3690
14 - 4	2638	0.3694			

t_+(ave.) = 0.3695, σ = 0.0004,

t_+(corr.)= 0.3692.

$LiNO_3$ (0.019302 M at -45.0°C.) I = 0.7027 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2218	0.3723	15 - 2	3609	0.3723
17 - 8	2495	0.3722	15 - 1	3886	0.3722
17 - 7	2770	0.3730	14 - 6	2219	0.3726
17 - 6	3049	0.3730	14 - 5	2496	0.3727
17 - 5	3326	0.3730	14 - 4	2776	0.3726
17 - 4	3606	0.3730	14 - 3	3053	0.3723
17 - 3	3883	0.3726	14 - 2	3331	0.3727
17 - 2	4161	0.3727	14 - 1	3608	0.3722
17 - 1	4438	0.3725	13 - 5	2218	0.3732
16 - 8	2217	0.3722	13 - 4	2498	0.3731
16 - 7	2492	0.3731	13 - 3	2775	0.3727
16 - 6	2771	0.3731	13 - 2	3053	0.3728
16 - 5	3048	0.3731	13 - 1	3330	0.3724
16 - 4	3328	0.3730	12 - 4	2221	0.3732
16 - 3	3605	0.3727	12 - 3	2498	0.3727
16 - 2	3883	0.3728	12 - 2	2776	0.3727
16 - 1	4160	0.3725	12 - 1	3053	0.3724
15 - 7	2218	0.3726	11 - 3	2220	0.3730
15 - 6	2497	0.3726	11 - 2	2498	0.3730
15 - 5	2774	0.3727	11 - 1	2775	0.3726
15 - 4	3054	0.3727	10 - 2	2222	0.3729
15 - 3	3331	0.3723	10 - 1	2499	0.3725

t_+(ave.) = 0.3727, σ = 0.0003,

t_+(corr.)= 0.3724.

$LiNO_3$ (0.10355 M at -65.0°C.) I = 3.584 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2522	0.3444	15 - 2	4104	0.3444
17 - 8	2838	0.3442	15 - 1	4420	0.3442
17 - 7	3150	0.3451	14 - 6	2522	0.3449
17 - 6	3467	0.3451	14 - 5	2840	0.3446
17 - 5	3785	0.3449	14 - 4	3157	0.3447
17 - 4	4102	0.3449	14 - 3	3473	0.3447
17 - 3	4418	0.3445	14 - 2	3789	0.3446
17 - 2	4743	0.3446	14 - 1	4105	0.3441
17 - 1	5050	0.3444	13 - 5	2525	0.3448
16 - 8	2524	0.3439	13 - 4	2842	0.3449
16 - 7	2836	0.3449	13 - 3	3158	0.3444
16 - 6	3153	0.3449	13 - 2	3474	0.3447
16 - 5	3471	0.3447	13 - 1	3790	0.3442
16 - 4	3788	0.3447	12 - 4	2527	0.3450
16 - 3	4104	0.3444	12 - 3	2843	0.3445
16 - 2	4420	0.3445	12 - 2	3159	0.3446
16 - 1	4736	0.3442	12 - 1	3475	0.3442
15 - 7	2519	0.3451	11 - 3	2528	0.3445
15 - 6	2836	0.3451	11 - 2	2844	0.3447
15 - 5	3154	0.3450	11 - 1	3160	0.3443
15 - 4	3471	0.3444	10 - 2	2527	0.3449
15 - 3	3787	0.3448	10 - 1	2843	0.3444

t_+(ave.) = 0.3446, σ = 0.0003,

t_+(corr.)= 0.3443.

$LiNO_3$ (0.051848 M at -65.0°C.) I = 1.7933 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2451	0.3547	15 - 2	3991	0.3544
17 - 8	2758	0.3544	15 - 1	4298	0.3543
17 - 7	3063	0.3551	14 - 6	2454	0.3547
17 - 6	3371	0.3551	14 - 5	2762	0.3545
17 - 5	3679	0.3550	14 - 4	3069	0.3548
17 - 4	3986	0.3551	14 - 3	3378	0.3542
17 - 3	4295	0.3546	14 - 2	3684	0.3547
17 - 2	4601	0.3547	14 - 1	3991	0.3541
17 - 1	4908	0.3545	13 - 5	2456	0.3548
16 - 8	2454	0.3540	13 - 4	2763	0.3550
16 - 7	2759	0.3547	13 - 3	3072	0.3543
16 - 6	3067	0.3548	13 - 2	3378	0.3547
16 - 5	3375	0.3547	13 - 1	3685	0.3543
16 - 4	3682	0.3549	12 - 4	2457	0.3551
16 - 3	3992	0.3543	12 - 3	2766	0.3543
16 - 2	4297	0.3546	12 - 2	3072	0.3546
16 - 1	4604	0.3542	12 - 1	3379	0.3543
15 - 7	2453	0.3547	11 - 3	2459	0.3545
15 - 6	2761	0.3547	11 - 2	2765	0.3547
15 - 5	3069	0.3547	11 - 1	3072	0.3544
15 - 4	3376	0.3548	10 - 2	2457	0.3550
15 - 3	3685	0.3543	10 - 1	2764	0.3546

t_+(ave.) = 0.3546, σ = 0.0003,

t_+(corr.)= 0.3543.

$LiNO_3$ (0.022810 M at -65.0°C.) I = 0.8031 mA.

Marks	Time	t_+	Marks	Time	t_+
17 - 9	2355	0.3626	15 - 2	3821	0.3636
17 - 8	2648	0.3626	15 - 1	4115	0.3634
17 - 7	2942	0.3632	14 - 6	2351	0.3636
17 - 6	3236	0.3634	14 - 5	2646	0.3635
17 - 5	3531	0.3634	14 - 4	2939	0.3639
17 - 4	3824	0.3637	14 - 3	3232	0.3636
17 - 3	4117	0.3634	14 - 2	3526	0.3640
17 - 2	4411	0.3635	14 - 1	3820	0.3634
17 - 1	4705	0.3633	13 - 5	2351	0.3641
16 - 8	2354	0.3624	13 - 4	2646	0.3641
16 - 7	2648	0.3631	13 - 3	2937	0.3640
16 - 6	2942	0.3634	13 - 2	3231	0.3643
16 - 5	3237	0.3633	13 - 1	3525	0.3638
16 - 4	3530	0.3637	12 - 4	2358	0.3642
16 - 3	3823	0.3634	12 - 3	2642	0.3641
16 - 2	4117	0.3636	12 - 2	2937	0.3643
16 - 1	4411	0.3633	12 - 1	3230	0.3640
15 - 7	2352	0.3634	11 - 3	2352	0.3640
15 - 6	2646	0.3637	11 - 2	2646	0.3641
15 - 5	2941	0.3635	11 - 1	2938	0.3640
15 - 4	3234	0.3639	10 - 2	2352	0.3643
15 - 3	3527	0.3636	10 - 1	2644	0.3640

t_+(ave.) = 0.3636, σ = 0.0004,

t_+(corr.)= 0.3633.

KI (0.050010 M at-68.0°C.) I = 1.5040 mA.

Marks	Time	t_+
17 - 5	3143	0.4779
17 - 4	3408	0.4778
17 - 3	3667	0.4777
16 - 5	2880	0.4781
16 - 4	3143	0.4782
16 - 3	3405	0.4777
15 - 5	2619	0.4780
15 - 4	2880	0.4784
15 - 3	3142	0.4779
14 - 5	2356	0.4780
14 - 4	2619	0.4782
14 - 3	2878	0.4781

t_+(ave.) = 0.4780

t_+(corr.)= 0.4776.

APPENDIX II

Variation of the density of liquid ammonia with temperature.

The following data have been calculated from the data of Cragoe and Harper (59) who presented the temperature dependency of the density as,

$$d = 0.6386 - 0.00134t - 0.0000013\overline{65}t^2$$

where t is expressed in °C.

Temp.(°C)	Density(g./ml.)	Temp.(°C)	Density(g./ml.)
-33	0.6813	-55	0.7082
-34	0.6826	-56	0.7093
-35	0.6838	-57	0.7106
-36	0.6850	-58	0.7117
-37	0.6862	-59	0.7129
-38	0.6875	-60	0.7141
-39	0.6887	-61	0.7152
-40	0.6900	-62	0.7165
-41	0.6912	-63	0.7176
-42	0.6924	-64	0.7188
-43	0.6937	-65	0.7199
-44	0.6950	-66	0.7211
-45	0.6961	-67	0.7223
-46	0.6973	-68	0.7234
-47	0.6986	-69	0.7245
-48	0.6998	-70	0.7257
-49	0.7010	-71	0.7268
-50	0.7022	-72	0.7280
-51	0.7033	-73	0.7291
-52	0.7046	-74	0.7303
-53	0.7058	-75	0.7314
-54	0.7070	-76	0.7325

All the results quoted in this table can be taken with confidence to 0.0002.

APPENDIX III

Calibration of the transference cell (see Experimental Section III.1)

Mark	Mark reading (cm.)	Distance between marks (cm.)	Meniscus reading (cm.)	Distance between meniscus readings (cm.)	Wt. of mercury (g.)	Wt. of mercury per cm. (g.)	Volume between marks (ml.)
1	84.235		84.233				
		0.500		0.503	0.52622	1.0461	0.038633
2	83.735		83.730				
		0.509		0.544	0.56671	1.0417	0.039163
3	83.226		83.186				
		0.501		0.501	0.52180	1.0415	0.038540
4	82.725		82.685				
		0.513		0.496	0.51459	1.0375	0.039311
5	82.212		82.189				
		0.505		0.510	0.53410	1.0473	0.039064
6	81.705		81.679				
		0.513		0.502	0.52002	1.0359	0.039251
7	81.192		81.177				
		0.513		0.505	0.52692	1.0434	0.039539
8	80.689		80.672				
		0.504		0.516	0.53800	1.0426	0.038812
9	80.185		80.156				
		0.506		0.493	0.51578	1.0462	0.039100
10	79.679		79.663				
		0.508		0.528	0.54829	1.0384	0.038962
11	79.171		79.135				
		0.505		0.481	0.50138	1.0424	0.038881
12	78.666		78.654				
		0.503		0.528	0.55272	1.0468	0.038890
13	78.163		78.126				
		0.508		0.496	0.51137	1.0310	0.038684
14	77.655		77.630				
		0.509		0.496	0.51660	1.0415	0.039155
15	77.146		77.134				
		0.507		0.462	0.48079	1.0407	0.038972
16	76.639		76.672				
		0.511		0.564	0.58401	1.0355	0.039083
17	76.128		76.108				
		0.506		0.478	0.49799	1.0418	0.038936
18	75.622		75.630				

Temperature of the calibration = 22°C.

Density of mercury (86) = 13.539 g./ml.

Calibration table for the calculation of the results in Appendix I.

(see Experimental Section III.1)

Marks	Volume	Marks	Volume	Marks	Volume
17 - 9	0.31173	16 - 2	0.54643	13 - 5	0.31249
17 - 8	0.35054	16 - 1	0.58495	13 - 4	0.35180
17 - 7	0.39007	15 - 7	0.31202	13 - 3	0.39035
17 - 6	0.42932	15 - 6	0.35127	13 - 2	0.42970
17 - 5	0.46839	15 - 5	0.39033	13 - 1	0.46814
17 - 4	0.50770	15 - 4	0.42965	12 - 4	0.31291
17 - 3	0.54624	15 - 3	0.46819	12 - 3	0.35145
17 - 2	0.58540	15 - 2	0.50727	12 - 2	0.39062
17 - 1	0.62403	15 - 1	0.54598	12 - 1	0.42925
16 - 8	0.31145	14 - 6	0.31212	11 - 3	0.31258
16 - 7	0.35099	14 - 5	0.35118	11 - 2	0.35174
16 - 6	0.39024	14 - 4	0.39049	11 - 1	0.39037
16 - 5	0.42931	14 - 3	0.42903	10 - 2	0.31278
16 - 4	0.46862	14 - 2	0.46859	10 - 1	0.35141
16 - 3	0.50716	14 - 1	0.50683		

(All volumes are recorded in ml.)

APPENDIX IV

Calibration of the standard flask.

Temperature of calibration = 23.8°C.

Atmospheric pressure = 755 mm. Hg.

Weight of the flask filled to the lowest mark with water

= 280.245 g.;

Weight of the flask in air = 141.950 g.;

Apparent weight of water = 138.621 g.;

Appox. volume of the flask = 138.9 ml.

thus the weight of air in the flask when weighed in air

= 0.163 g.

Thus the weight of water in the flask when filled to the

lowest mark = 280.245 - (141.950 - 0.163)

= 138.458 g.,

and the volume of this water, the density (60) being taken as

0.997345 g./ml. at 23.8°C. = 138.83 ml.

The volume between two marks when the dip-pipe was not in position

= 0.150 ml.

The dimensions of the dip-pipe were; internal diameter, 0.180 cm.;

and external diameter, 0.344 cm.

The distances between the marks on the neck were 0.254 cm., therefore

the volume of the glass in the dip-pipe between two marks

$$= [(0.172)^2 - (0.090)^2]0.254\pi$$

= 0.017 ml.

Thus the volume of liquid between two adjacent marks

= 0.150 - 0.017

= 0.133 ml.

When the standard flask, filled to the lowest mark, was placed on the apparatus the liquid level rose by 8.5 marks. Therefore, the volume of glass in the dip-pipe up to the lowest mark

$$= 8.5 \times 0.133 \text{ ml.},$$

and when the dip-pipe was inserted the volume of liquid accommodated up to the lowest mark

$$= 138.83 - (8.5 \times 0.133)$$

$$= 137.70 \text{ ml. at } 33.8^{\circ}\text{C.}$$

At -55°C, the volume of the flask reduces by

$$137.70 \times 1.08 \times 10^{-5} \times 79$$

$$= 0.12 \text{ ml.}$$

(where 1.08×10^{-5} is the volume coefficient of expansion of Pyrex glass). Thus, at -55°C, the volume of the flask was taken as

$$= \underline{137.58} \text{ ml.}$$

and an additional 0.133ml. was added for each mark in the neck.

Two other similar determinations of the volume, at different times in the course of the work, gave volumes of 137.52 ml. and 137.59 ml.

APPENDIX V

The values of the saturated vapour pressure of ammonia over pure liquid ammonia given below are those given by Cragoe, Meyers and Taylor (91).

Temp.(°C)	S.V.P.(mm.Hg)	Temp.(°C)	S.V.P.(mm.Hg)
-78	44.3	-55	226.2
-77	48.0	-54	240.7
-76	51.9	-53	255.9
-75	56.1	-52	272.0
-74	60.6	-51	288.8
-73	65.5	-50	306.6
-72	70.6	-49	325.2
-71	76.1	-48	344.7
-70	81.9	-47	365.2
-69	88.1	-46	386.6
-68	94.7	-45	409.1
-67	101.8	-44	432.7
-66	109.2	-43	457.3
-65	117.1	-42	483.1
-64	125.4	-41	510.1
-63	134.3	-40	538.3
-62	143.7	-39	567.8
-61	153.7	-38	598.5
-60	164.2	-37	630.6
-59	175.3	-36	664.1
-58	187.0	-35	699.0
-57	199.4	-34	735.4
-56	212.5		

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ACKNOWLEDGEMENTS

The author wishes to thank the University of Edinburgh for the award of an Imperial Chemical Industries Research Fellowship during the tenure of which this work was carried out, and also Professors Sir Edmund Hirst and T. L. Cottrell for the provision of laboratory facilities in the Chemistry Department.

Thanks are also due to British Petroleum Limited for the supply of high purity liquid propane from their refinery at Grangemouth, and to Imperial Chemical Industries Limited for the loan of refrigeration equipment.

The author would also like to thank Mr. A. Young of the Department of Chemistry, University of Edinburgh, for constructing the constant current device which was used in this work.